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AN INVESTIGATION OF THE MECHANISM OF EXPLOSIVE REACTIONS

BY

CRANDALL Z. ROSECRANS

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ENGINEERING EXPERIMENT STATION

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RESEARCH ASSOCIATE, ENGINEERING EXPERIMENT STATION

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CONTENTS

PAGE

I. INTRODUCTION 7
1. Statement of Problem 7
2. Object and Scope of Investigation 7
3. Acknowledgments 7

II. THEORETICAL DISCUSSION OF EXPLOSIONS IN A CLOSED VESSEL 8
4. Process of Explosion 8
5. General Statement Regarding Theory 9
6. Derivation of Principal Equation 9
7. Derivation of Velocity Equations 14

III. CHEMICAL AND PHYSICAL PROPERTIES OF FUEL 16
8. Fuel Used in Experiments 16
9. Vapor Pressure 16
10. Specific Heat 17
11. Heat of Combustion 18
12. Ratio of Specific Heats 20

IV. EXPERIMENTAL APPARATUS 20
13. Explosion Apparatus 20
14. Bomb 20
15. Extension Cylinder 21
16. Heating Coil 21
17. Indicator 21
18. Recording Apparatus 21
19. Flame Photography 22
20. Ignition Apparatus 24
21. Timing Apparatus 25
22. Temperature and Pressure Measurement 25
23. Fuel Measurement and Charging 26

PAGE

V. Method of Conducting Experiments 26
24. Procedure in Making an Explosion 26
25. Calculation of Air: Fuel Ratio 27
26. Computation and Plotting of Pressure Curve . . . 28
27. Computation and Plotting of Flame Curve 29
28. Precision and Accuracy of Measurements 30

VI. Results 31
29. Comparison of Actual and Calculated Flame Curves . 31
30. Velocity of Flame Propagation 37
31. Flame Arrest 38
32. Character of Expansion and Compression of Gases during Explosion Process 41
33. Reaction Velocity 44
34. Gas Movements during Explosion 48

VII. Conclusions 48
35. Summary of Conclusions 48

Appendix A. Bibliography on Gaseous Explosions 50
1. General Statement 50

LIST OF FIGURES

NO.		PAGE
1.	Diagram of Explosion Process	8
2.	Diagram of Explosion Bomb	9
3.	Specific Heat Curve for Ethyl Ether	18
4.	General View of Explosion Apparatus	22
5.	Diagram of Recording Apparatus	23
6.	Multiple Gap Ignitor	25
7.	Flame Photograph for Test No. 4	28
8.	Indicator Diagram for Test No. 11	28
9.	Pressure and Flame Curves for Test No. 4	29
10.	Flame Photographs for Test Nos. 2, 3, 8, and 10	32
11.	Pressure and Flame Curves for Tests Nos. 1, 2, 3, and 4	34
12.	Pressure and Flame Curves for Tests Nos. 5, 6, 7, and 8	35
13.	Pressure and Flame Curves for Tests Nos. 9, 10, 11, and 12	36
14.	Curves of the Variation of the Values of m and n for Test No. 4	41
15.	Curves of the Variation of the Value of n for Tests Nos. 3, 5, 6, 9, 11, and 12	43
16.	Curve Showing the Division of Total Flame Velocity for Test No. 4	44
17.	Curve Showing Variation of Reaction Velocity with Pressure	45
18.	Curve Showing Variation of Slope of Reaction Velocity with Fuel Mixture	46
19.	Gas Movement Diagram for Test No. 4	47

LIST OF TABLES

NO.		PAGE
1.	Specific Heat of Ethyl Ether Vapor	17
2.	Calculations of Theoretical Analysis of Flame Propagation	33
3.	Test Data	37
4.	Flame Velocities	38
5.	Flame Arrest Data	39

AN INVESTIGATION OF THE MECHANISM OF EXPLOSIVE REACTIONS

I. Introduction

1. *Statement of Problem.*—The numerous changes in the composition of liquid fuels for internal combustion engines and the tendency towards the employment of higher compression ratios, which frequently result in "fuel knock," have indicated the desirability of a more detailed and complete knowledge of the actual mechanism of explosive reactions.

A great amount of experimental work has been done on this problem, but there are so many phases of the general subject that it is difficult to consider more than one or two divisions of the problem in one investigation.

The experiments reported in this bulletin are a continuation of the general investigation of the explosion of gaseous and liquid fuels which has been conducted in the Engineering Experiment Station of the University of Illinois.*

2. *Object and Scope of Investigation.*—The object of this investigation was a study of the flame propagation in a closed cylindrical bomb and a comparison of results of a theoretical analysis of flame propagation with the actual phenomena as observed by means of photographic records.

Furthermore, it was desired to investigate certain phenomena reported by other experimenters, such as the flame arrest and other obscure processes of explosive reaction.

The present investigation has been limited to the study of the explosion of mixtures of ethyl ether and air in a cylindrical bomb of constant volume. Two bombs of the same diameter but different lengths were used for the investigation.

3. *Acknowledgments.*—Acknowledgment is hereby made to A. P. Kratz, Research Professor in the Department of Mechanical Engineering, for his continued interest and helpful suggestions. Mr. A. G. Eldredge, Head of the Department of Photography, also made many valuable suggestions relative to the photographic processes and gave material assistance by the loan of photographic apparatus.

*"A Study of Explosions of Gaseous Mixtures," Univ. of Ill. Eng. Exp. Sta., Bul. 133, 1922.

II. Theoretical Discussion of Explosions in a Closed Vessel

4. *The Process of Explosion.*—If a homogeneous mixture of inflammable gas, or vapor, and air, at a given temperature and pressure, is enclosed in a vessel, and the mixture is ignited, the resultant reaction will take place at a rate dependent on various conditions existing in regard to the character of the fuel and to the physical state of the mixture. The reaction occurring in such a case may be classed as a progressive homogeneous reaction.*

The reaction proceeds somewhat as follows: Assuming ignition at one end of the bomb, a layer of gas near the ignition point burns and expands. On expanding, it compresses the unburned layers of gas as shown in Fig. 1. The second layer of gas mixture is ignited by contact and mechanical spread of the flame, and it in turn burns and expands, further compressing the unburned mixture ahead of it. This process is repeated until all the mixture in the bomb has burned. It is obvious from the process thus defined that each layer of gas burns under conditions different from those affecting the layer immediately before or immediately after it.

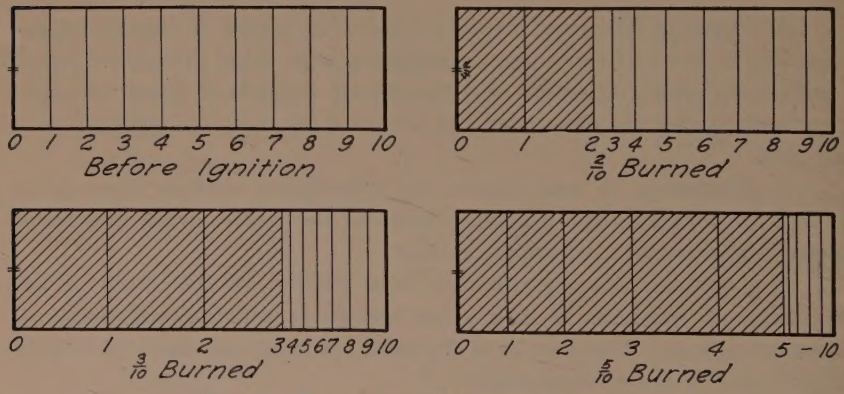

Fig. 1. Diagram of Explosion Process

A combustion such as described is what might be termed a "normal explosion," since it is not of the "slow combustion" type, which presumably occurs immediately after ignition, nor is it a detonation, which might be called an "abnormal explosion."

Even though the process of normal explosion is a progressive one and the reaction proceeds under different conditions from point to point,

*Brown, G. G. Ind. & Eng. Chem., Vol. 17, p. 1229, 1925.

an analysis can be made which takes into account the different initial conditions under which each gas layer burns. Such an analysis has been made by Professor A. Nägel* (see Section 6).

In order to calculate the maximum temperature and pressure attained (assuming the reaction to be homogeneous, not progressive, and to take place uniformly throughout the mixture), the method of Good-enough† has been used. This method takes into account the variations with temperature of the specific heat of the gases, and also the dissociation of the gases at high temperature.

5. *General Statement Regarding Theory.*—The theory upon which the calculation of flame propagation is based is that of Professor Nägel.* The derivations which follow are adapted from those given by Professor Nägel, and in addition some new relations have been deduced.

6. *Derivation of Principal Equation.*—Consider a closed cylindrical bomb, filled with a mixture of inflammable gas and air. Let the mixture be ignited at one end of the bomb, and let combustion proceed until a certain fraction of the original volume V is burned. This combustion is assumed to take place adiabatically and at constant volume. Now let the burned gas which is at high pressure and temperature expand adiabatically according to the equation

$$PV^k = \text{constant}$$

until pressure equilibrium within the bomb is attained. This process of constant volume adiabatic combustion and subsequent adiabatic expansion is then repeated, until the whole gas volume is burned.

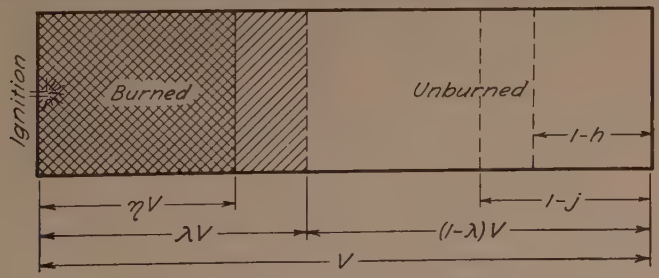

FIG. 2. DIAGRAM OF EXPLOSION BOMB

Figure 2 shows a diagrammatic sketch of the cylindrical explosion bomb, with the burned gas volume and the unburned gas volume. The figure represents the state of the gas after the constant volume adiabatic combustion and before expansion. The following notation will be used, assuming that V, the total volume of the bomb, is the volume of one mol of the initial gas mixture:

*Nägel, A., "Versuche über die Zündgeschwindigkeit explosiber Gasgemische," Mitteilungen ü. Forschungsarbeiten, Vol. 54, pp. 1-42, 1908.

†"An Investigation of the Maximum Temperatures and Pressures Attainable in the Combustion of Gaseous and Liquid Fuels," Univ. of Ill. Eng. Exp. Sta. Bul. 139, 1923.

Notation

Volume I Burned	Volume II Unburned
Before Combustion	*Before Compression*
Pressure = P_1	Pressure = P_1
Temperature = T_1	Temperature = T_1
Volume = $\eta\, V$	Volume = $(1 - \eta)\, V$
Weight = η	Weight = $(1 - \eta)$
After Combustion	
Pressure = P_v	
Temperature = T_v	
Volume = $\eta' V$	
Weight = η'	
After Expansion	*After Compression*
Pressure = P''	Pressure = P''
Temperature = T''	Temperature = T'
Volume = $\lambda\, V$	Volume = $(1 - \lambda)\, V$
Weight = η'	Weight = $(1 - \eta)$

The whole process is assumed to be adiabatic. Hence the decrease in energy of the volume I caused by the adiabatic expansion is equal to the increase in energy of the volume II caused by the adiabatic compression. Or,

$$\eta'\, \gamma_v''\, (T_v - T'') = (1 - \eta)\, \gamma_v'\, (T' - T_1) \tag{1}$$

where γ_v'' and γ_v' represent respectively the specific heats at constant volume of the burned and unburned gases. If γ_1 denotes the ratio $\frac{\gamma_v''}{\gamma_v'}$, then

$$\gamma_1\, \eta'\, (T_v - T'') = (1 - \eta)\, (T' - T_1) = (1 - \eta)\, T_1 \left(\frac{T'}{T_1} - 1 \right) \tag{2}$$

From the equation for adiabatic changes of volume,

$$\frac{T'}{T_1} = \left(\frac{P''}{P_1} \right)^{\frac{k-1}{k}} = \Pi^{\frac{k-1}{k}} \tag{3}$$

where Π is the ratio of the final pressure P'' to the initial pressure P_1. Substituting in (2)

$$\gamma_1 \eta' (T_v - T'') = (1 - \eta) T_1 (\Pi^{\frac{k-1}{k}} - 1)$$

$$\text{or } \frac{1-\eta}{\eta'}\left[\Pi^{\frac{k-1}{k}} - 1\right] = \frac{\gamma_1 T_v}{T_1}\left(1 - \frac{T''}{T_v}\right) \tag{4}$$

Applying the law for perfect gases to the various volumes

$$P_1 \eta V = \eta R T_1 \tag{5}$$

$$P_v \eta V = \eta' R T_v \tag{6}$$

$$P'' \lambda V = \eta' R T'' \tag{7}$$

From these equations

$$\eta' = \eta \frac{P_v T_1}{P_1 T_v} = \eta \Pi_v \frac{T_1}{T_v} \tag{8}$$

$$\eta' = \lambda \frac{P'' T_1}{P_1 T''} = \lambda \Pi \frac{T_1}{T''} \tag{9}$$

Dividing (8) by (9)

$$\frac{T''}{T_v} = \frac{\lambda \Pi}{\eta \Pi_v} \tag{10}$$

Substituting (10) in (4)

$$\frac{1-\eta}{\eta'}\left[\Pi^{\frac{k-1}{k}} - 1\right] = \frac{\gamma_1 T_v}{T_1}\left(1 - \frac{\lambda \Pi}{\eta \Pi_v}\right) \tag{11}$$

Substituting the value of η' given by (8) in (11)

$$\frac{1-\eta}{\eta}\left[\Pi^{\frac{k-1}{k}} - 1\right] = \gamma_1 \Pi_v - \gamma_1 \frac{\lambda \Pi}{\eta} \tag{12}$$

Let $\frac{1}{\gamma_1} = \gamma$. Then

$$\gamma \frac{1-\eta}{\eta}\left[\Pi^{\frac{k-1}{k}} - 1\right] + \frac{\lambda \Pi}{\eta} = \Pi_v$$

By adding and substracting Π and Π_v in the preceding equation, the following is obtained:

$$\gamma (1 - \eta) \left[\Pi^{\frac{k-1}{k}} - 1 \right] - \Pi (1 - \lambda) + \Pi = -\Pi_v (1 - \eta) + \Pi_v \quad (13)$$

Applying the equation for adiabatic compression to the unburned gas

$$\frac{(1 - \lambda) V}{(1 - \eta) V} = \left(\frac{P_1}{P''} \right)^{\frac{1}{k}} = \Pi^{-\frac{1}{k}} \quad (14)$$

to (13)

$$(1 - \lambda) \left[\gamma \left(\Pi - \Pi^{\frac{1}{k}} \right) - \Pi + \frac{\Pi_v}{\Pi^{\frac{1}{k}}} \right] = \Pi_v - \Pi$$

and simplifying

$$1 - \lambda = \frac{\Pi_v - \Pi}{\Pi^{\frac{1}{k}} (\Pi_v - \gamma) - \Pi (1 - \gamma)} \quad (15)$$

Equation (15) is the principal equation for the progress of the combustion. It expresses λ, the travel of the flame along the bomb, in terms of the pressure attained Π, the maximum pressure of adiabatic constant volume combustion Π_v, and the constants of the gas, γ and k.

It should be noted that the exponent k, which appears in equation (15), results from a consideration of the compression of the unburned gas volume only.

It is evident that the basis of this theory is found in equation (1), where the changes in energy of the two gas volumes caused by their respective expansion and compression are equated. If the process is not adiabatic, or if the reaction continues during and after the expansion of the burned gas, the equality of the two energy changes naturally is not valid.

However, a considerable amount of information can be obtained by assuming the equality of the energy changes, and by calculating the values of the exponent n in the equation.

$$PV^n = \text{constant}$$

from equation (15). That is, it may be assumed that equation (15) is valid, even though the process is not adiabatic, and in place of the constant k, the value n may be substituted. Equation (15) then becomes

$$1 - \lambda = \frac{\Pi_v - \Pi}{\Pi^{\frac{1}{n}} (\Pi_v - \gamma) - \Pi (1 - \gamma)} \tag{16}$$

Solving equation (16) for n,

$$n = \frac{\log \Pi}{\log \left[\frac{\Pi_v - \Pi}{(\Pi_v - \gamma)(1 - \lambda)} + \frac{\Pi (1 - \gamma)}{(\Pi_v - \gamma)} \right]} \tag{17}$$

By substituting known values of λ and Π from the curves of flame propagation and pressure, determined by experiment, a value of n can be obtained. This value of n will vary thoroughout the explosion process, and while its value in the strictest sense is subject to question, its variation will throw some light on the processes occurring during explosion.

If it is assumed that the burned gases expand according to the law PV^m = constant (instead of PV^k = constant), where m is a variable during the explosion, the value of m can be determined as follows:

From a consideration of the pressures and volumes of gas

$$P_v \eta^m = P'' \lambda^m \tag{18a}$$

$$P_1 (1 - \eta)^n = P'' (1 - \lambda)^n \tag{18b}$$

$$\Pi_v^{\frac{1}{m}} \eta = \Pi^{\frac{1}{m}} \lambda \tag{18c}$$

$$(1 - \eta) = \Pi^{\frac{1}{n}} (1 - \lambda) \tag{18d}$$

Substituting η from equation (18d) in equation (18c)

$$\Pi_v^{\frac{1}{m}} \left[1 - \Pi^{\frac{1}{n}} (1 - \lambda) \right] = \Pi^{\frac{1}{m}} \lambda$$

and solving for m,

$$m = \frac{\log \frac{\Pi_v}{\Pi}}{\log \left[\frac{\lambda}{1 - \Pi^{\frac{1}{n}} (1 - \lambda)} \right]} \tag{19}$$

It is obvious that the value of m, determined as above, is subject to the same criticism as that of n, determined before, since equation (19), evaluating m, also contains n. However, as in the case of n, the variation of m is of sufficient significance to warrant the drawing of conclusions from it.

7. *Derivation of Velocity Equations.*—The velocity with which the flame proceeds is composed of two components:

(1) The chemical reaction velocity, or the velocity with which the reaction progresses from one molecule to the next.

(2) The "compression" velocity, or the velocity of forward motion of the molecules caused by the compression of the unburned gas ahead of the flame front.

The total flame velocity is found by differentiating equation (15) with respect to time. The total velocity is Ψ, and is expressed by

$$\Psi = \frac{d\lambda}{dt}$$

$$= \frac{\Pi^{\frac{1}{n}}(\Pi_v - \gamma) - \Pi(1-\gamma) + (\Pi_v - \Pi)\left[(\Pi_v - \gamma)^{\frac{1}{n}}\left(\frac{1}{\Pi}\right)^{\frac{n-1}{n}} - (1-\gamma)\right]\frac{d\Pi}{dt}}{\left[\Pi^{\frac{1}{n}}(\Pi_v - \gamma) - \Pi(1-\gamma)\right]^2} \qquad (20)$$

$\frac{d\Pi}{dt}$ can be determined from the indicator diagram. All the other quantities appearing in equation (20) are determined from experimental data, and therefore the total flame velocity Ψ can be found.

The velocity of forward motion of the unburned gas immediately in front of the flame is to be determined next. Referring to Fig. 2, $(1-j)$ denotes the volume of a certain quantity of unburned gas before the adiabatic compression has occurred, and $(1-h)$ denotes the volume of the same quantity of gas after the adiabatic compression. Applying the equation for adiabatic compression, analogous to equation (14),

$$\frac{1-h}{1-j} = \Pi^{-\frac{1}{n}}$$

or

$$1 - h = \frac{1-j}{\Pi^{\frac{1}{n}}} \qquad (21)$$

Differentiating equation (21) with respect to time, the velocity of forward motion of the unburned gas at the point denoted by $(1-h)$ in Fig. 2 is found.

$$\frac{dh}{dt} = \frac{dh}{d\Pi}\frac{d\Pi}{dt} = \frac{1}{n}(1-j)\left(\frac{1}{\Pi}\right)^{\frac{n+1}{n}}\frac{d\Pi}{dt} \tag{21a}$$

If the distance $(1-h)$ is made equal to $(1-\lambda)$, thus making the volume $(1-h)$ equal to the volume $(1-\lambda)$, and $(1-j)$ becomes $(1-\eta)$, then the velocity of forward motion of the unburned gases immediately in front of the flame is

$$\Psi' = \frac{d\lambda'}{dt} = \frac{d\lambda'}{d\Pi}\frac{d\Pi}{dt} = \frac{1}{n}(1-\eta)\left(\frac{1}{\Pi}\right)^{\frac{n+1}{n}}\frac{d\Pi}{dt} \tag{22}$$

where $\frac{d\lambda'}{dt}$ denotes the velocity of the unburned gas, as differentiated from $\frac{d\lambda}{dt}$, the total flame velocity.

Let the subscript z denote the application of equations (20) and (22) to a layer of gas at the instant of its entry into the flame front, or zone of combustion. Then η becomes η_z, denoting a given distance along the bomb at which the velocities are to be investigated; $\Pi, \frac{d\Pi}{dt}$, λ, and other quantities are to be taken for this point.

The chemical reaction velocity, or the velocity with which the reaction progresses from one molecule to the next, is then

$$\Psi_{ch} = \Psi_z - \Psi_z' \tag{23}$$

In order to simplify the calculation of the chemical reaction velocity, the quotient of the total flame velocity and the velocity of the forward motion of the unburned gas is first derived.

$$\frac{\Psi_z}{\Psi_z'} = \frac{\Psi_z' + \Psi_{ch}}{\Psi_z'}$$

$$= \frac{n\Pi^{\frac{n+1}{n}}\left\{\Pi^{\frac{1}{n}}(\Pi_v-\gamma)-\Pi(1-\gamma)+(\Pi_v-\Pi)\left[\frac{1}{n}(\Pi_v-\gamma)\left(\frac{1}{\Pi}\right)^{\frac{n-1}{n}}-(1-\gamma)\right]\right\}}{\left[\Pi^{\frac{1}{n}}(\Pi_v-\gamma)-\Pi(1-\gamma)\right]^2(1-\eta')} \tag{24}$$

From equation (14)

$$1-\eta' = (1-\lambda)\,\Pi^{\frac{1}{n}} \tag{25}$$

Combining equation (14) with equation (15)

$$1 - \eta' = \frac{\Pi_v - \Pi}{\Pi^{-\frac{1}{n}}\left[\Pi^{\frac{1}{n}}(\Pi_v - \gamma) - \Pi(1 - \gamma)\right]} \tag{26}$$

Substituting in equation (24) and simplifying,

$$\frac{\Psi_z}{\Psi'_z} = 1 + \frac{n}{\frac{\Pi_v}{\Pi} - 1} - \frac{\Pi(n-1)(1-\gamma)}{\Pi^{\frac{1}{n}}(\Pi_v - \gamma) - \Pi(1-\gamma)} \tag{27}$$

As an approximation the last term can be neglected, since $(n - 1)$ and $(1 - \gamma)$ are both less than unity, and since the two terms in the denominator are fairly large. Then

$$\frac{\Psi_z}{\Psi_z'} = \frac{\Psi_z' + \Psi_{ch}}{\Psi_z'} = 1 + \frac{\Psi_{ch}}{\Psi_z'} = 1 + \frac{n}{\frac{\Pi_v}{\Pi} - 1} \tag{28}$$

expresses the ratio of the total flame velocity to the velocity of forward motion of the unburned gas in terms of known quantities. The relative proportion of the total flame velocity which is due to chemical reaction velocity is then

$$\frac{\Psi_{ch}}{\Psi_z} = 1 - \frac{\Psi_z'}{\Psi_z} = 1 - \frac{1}{1 + \frac{n}{\frac{\Pi_v}{\Pi} - 1}} \tag{29}$$

and the chemical reaction velocity may be determined.

III. Chemical and Physical Properties of Fuel

8. *Fuel Used in Experiments.*—The fuel used in the experiments was ethyl ether (technically pure). This fuel was selected because its high vapor pressure afforded an opportunity of making explosions over a greater range of temperatures at given initial pressures than if some more common paraffin fuel, such as gasoline, had been used.

The general properties and constants of the ethyl ether fuel are discussed below.

9. *Vapor Pressure.*—A knowledge of the vapor pressure of ether at various temperatures was necessary, in order that the temperatures for various initial bomb pressures might be so chosen that the fuel would be completely vaporized.

From the results of Young* the vapor pressures are as follows:

*Proc. Royal Dublin Society, Vol. 12, p. 374, 1909-10.

VAPOR PRESSURES OF ETHYL ETHER

Temperature deg. F.	Vapor Pressure lb. per sq. in.
104	17.78
122	24.63
158	44.50
212	93.80
266	176.8
302	256.3

10. *Specific Heat.*—The available data on the specific heat of ethyl ether vapor are so few that only an approximation can be made relative to the variation of the specific heat of ether vapor with pressure. Hence, the approximate equation given below is probably as valid as any, considering the data available.

Wiedemann* gives for the mean specific heat of ether vapor at constant pressure

25–111 deg. C.	31.7 (per mol)
27–189 deg. C.	34.2 (per mol)

Regnault's value† between the temperatures of 69 and 224 deg. C. is 35.6 for γ_p, the specific heat per mol at constant pressure.

De Heen‡ gives for γ_p at 185 deg. C. the value 40.5.

Converting to Fahrenheit temperatures, the following table is obtained:

TABLE 1.

SPECIFIC HEAT OF ETHYL ETHER VAPOR

Mean Temperatures			Specific Heat at Constant Pressure
deg. C	deg. F.	deg. F. abs.	B.t.u. per lb. mol.
68	154.4	614.0	31.7
108	226.4	686.0	34.2
146	294.8	754.4	35.6
185	365.0	824.6	40.5

*Wied. Ann., vol. 2, p. 195, 1877.
†Mem. de l'Acad., vol. 26, p. 1, 1862.
‡Bul. de Belg., ser. 3, vol. 15, p. 522, 1888. Phil. Mag., ser. 5, vol. 26, p. 467, 1888.

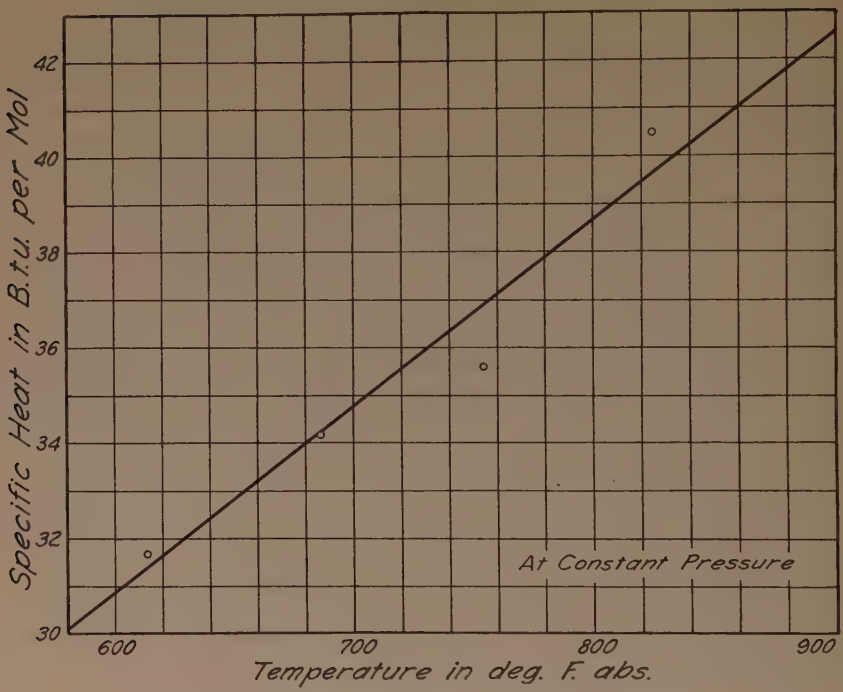

FIG. 3. SPECIFIC HEAT CURVE FOR ETHYL ETHER

These values are plotted in Fig. 3. A straight line relation between specific heat and temperature is assumed, as shown. The specific heat equations are then

$$\gamma_p = 8.820 + 0.0367\ T$$
$$\gamma_v = 6.835 + 0.0367\ T$$

where T denotes the temperature in deg. F. abs., and γ_p and γ_v are the specific heats per mol at constant pressure and constant volume, respectively.

11. *Heat of Combustion.*—The heat of combustion of ethyl ether vapor is given by Thomsen* as 659.6 kg. cal. per gm. at 18 deg. C. The ether was burned at constant pressure and the water in the products of combustion condensed. Correcting to the lower heating value† and reducing to heat of combustion in B.t.u. per lb. mol, the value 1 131 029 B.t.u. is obtained. Or, at constant volume, the lower heat of combustion is (at 64.4 deg. F. or 524 deg. F. abs.)

*"Thermochemische Untersuchungen," vol. IV, p. 147. 1886.
†Univ. of Ill. Eng. Exp. Sta. Bul. 139, p. 110.

$$H_v = 1\ 133\ 109 \text{ B.t.u. per lb. mol}$$

Stohmann* gives 660.175 kg. cal. per gm. mol at 18 deg. C. as the heat of combustion at constant pressure. In the determination of this value the ether was burned as vapor, and the water in the products of combustion was condensed. Correcting this value as before, the lower heat of combustion at constant pressure and at 18 deg. C. is found to be

$$H_p = 1\ 132\ 063 \text{ B.t.u. per lb. mol}$$

The heat of combustion at constant volume is then

$$H_v = 1\ 134\ 143 \text{ B.t.u. per lb. mol}$$

at 64.4 deg. F. or 524 deg. F. abs.

Taking the mean of the values according to Thomsen and Stohmann, the heating value is

$$H_v = 1\ 133\ 626 \text{ B.t.u. per lb. mol}$$

at 524 deg. F. abs.

In order to obtain an expression for the variation of H_v with temperature, an expression derived in Bulletin No. 139† was used.

$$H_v = H_o + T\left(\sigma' + \tfrac{1}{2}\,\sigma''\,T + T + \tfrac{1}{3}\,\sigma'''\,T^2\right) - n\,R\,T$$

Substituting the known values of H_v, σ, and T in this equation, H_o was calculated, and the final equation then became

$$H_v = 1\ 139\ 198 - 15.88\,T + 0.0103\,T^2 - 0.55 \times 10^{-6}\,T^3$$

Values of H_v for various temperatures were calculated from this equation, as follows:

T deg. F. abs.	H_v
500	1 133 763
1200	1 134 026

It is evident that the change in value of H_v over the range from 500 to 1200 deg. F. abs. is a very small amount as compared with the total value. Therefore, H_v has been considered as a constant in the range from 500 to 1200 deg. F. abs., and is taken as

$$H_{v_{520}} = 1\ 133\ 800 \text{ B.t.u. per lb. mol}$$

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*Jour. prakt. Chem., ser. 2, vol. 35, p. 140, 1887.
†*Loc. cit.*, p. 19, equation (12).

12. *Ratio of Specific Heats.*—For air, the ratio of the specific heats at constant pressure and constant volume is

$$k = \frac{\gamma_p}{\gamma_v} = 1.40^*$$

For ethyl ether at 212 deg. F.

$k = 1.11$ Stevens†
$k = 1.08$ Cazin‡

The value adopted for k for ethyl ether was 1.10. To conform strictly to actual conditions, values of k at the actual temperatures and pressures existing in the gas about to undergo combustion should be used. However, data on the value of k under high temperature and pressure conditions were lacking, and the best available values seemed to be those at 212 deg. F.

IV. Experimental Apparatus

13. *Explosion Apparatus.*—The apparatus consisted of a closed steel bomb, an ignition system, a motion picture camera, an indicator camera, a pressure indicator, a thermocouple system, and an auxiliary apparatus for charging the fuel into the bomb.

14. *Bomb.*—The explosion bomb was a cylindrical vessel of steel, 4 inches inside diameter, and 15 inches long, having a volume of 197.3 cu. in. including the various connections. It was made with very heavy walls, approximately 2½ inches thick. The inner surface was machined to a smooth finish, but owing to the difficulty of cleaning, it soon became corroded, and for all the tests was in approximately the same condition.

An opening in the top of the bomb (Fig. 5) provided a means for introducing the fuel. Two heavy needle valves, located at one side of the bomb, were used to charge the bomb to any desired initial pressure, and to exhaust or scavenge it. The cylinder heads, of cast steel, were held in place by 1-inch stud bolts. One head was furnished with a hole for the optical indicator connection, and the other with holes for the spark plug and insulated electrical connections. A slit, ⅜ inch wide and extending along an element of the cylinder, was closed by a piece of crystal glass ¾ inch thick, ground and polished. The glass was

*The commonly used value, which is the mean of a number of determinations, at 212 deg. F.
†Stevens, Annalen der Physik, ser. 4, vol. 7, p. 285, 1902.
‡Cazin, Ann. chim. phys., ser. 3, vol. 66, p. 206, 1862.

packed in place between rubber gaskets, and was clamped by heavy steel clamp plates extending along each side.

15. *Extension Cylinder.*—For certain tests it was desirable to use a cylinder of greater length than that of the main bomb. Accordingly, an extension cylinder, of cast steel, was bolted to one end of the main bomb. This extension cylinder was of the same internal diameter as the main bomb (4 inches) and was 7.5 inches long. When bolted to the end of the main bomb the assembly furnished a cylinder 22.5 inches long, with the glass window extending along the side from 9.0 inches to 21.0 inches (assuming zero at the spark plug end of the bomb). The extension cylinder was not provided with a glass window. A thermocouple was inserted through an insulated bushing in the extension cylinder.

16. *Heating Coil.*—In order to heat the whole bomb to temperatures above the boiling point of the fuels used, it was wound with No. 18 chromel wire. The wire was insulated from the cylinder by slipping it through ½-inch lengths of porcelain tubing, ¼ inch in outside diameter. The wire was wound from a transite strip attached to the cylinder close to the glass window, around the bomb, to a corresponding transite strip on the other side of the window, and reverse. In this way the whole available surface of the cylinder except the window was wound with wire. A wooden box was built around the bomb, leaving the window and ends exposed. The box was then filled with shredded asbestos and magnesia insulation. The heating coil proved to be very satisfactory, and no trouble was experienced in securing the desired temperature or in maintaining it practically constant.

17. *Indicator.*—The indicator used was of the optical type, employing a diaphragm as a spring. This same instrument was used in a previous investigation of gaseous explosions.* A calculation for the natural period of vibration of the diaphragm proved that the period was very short as compared with the time of the explosions and led to the conclusion that the instrument could follow the most rapid variations in pressure which were likely to occur. The indicator was calibrated in place by means of a dead-weight gage tester.

18. *Recording Apparatus.*—A photograph of the recording apparatus is shown in Fig. 4, and a diagrammatic sketch of the whole apparatus in Fig. 5. The apparatus was driven by a small direct-current motor, equipped with a sensitive speed control. The recording films were held on film drums similar to standard oscillograph film drums. These drums

*Univ. of Ill. Eng. Exp. Sta. Bul. 133, pp. 16-19, 1922.

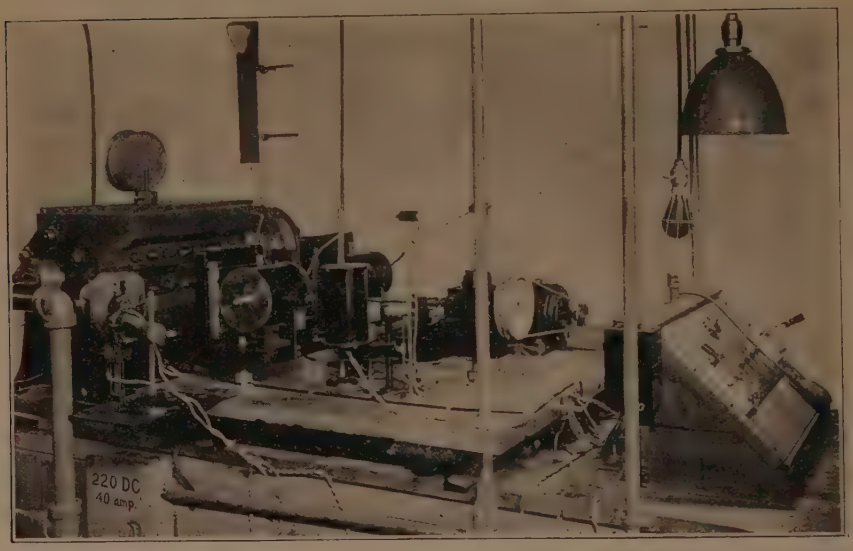


FIG. 4. GENERAL VIEW OF EXPLOSION APPARATUS

were rotated by the motor through the worm drive, as shown in Fig. 5. The drum casings (light-tight) were equipped with bakelite spark plugs containing spark gaps which were connected in series with the ignition gap in the explosion bomb. By means of these series spark gaps a mark was made on each film at the instant of the passage of the spark in the bomb, thereby furnishing a means of correlating the various records obtained on the films with the process taking place in the bomb.

A photographic shutter placed in front of the indicator film drum was used to protect the film from the light until the time of taking the record. Standard Eastman photographic film was used for making the indicator records.

19. *Flame Photography.*—The flame of the explosion was photographed as it appeared through the $\frac{3}{8}$-inch wide slit along the explosion bomb. An F:1.9 motion picture lens of 41 mm. focal length was used to focus the image of the slit on the film. The film was carried on the film drum, which rotated past the lens; thus the image of the slit, if illuminated, produced a continuous strip photograph on the film. The relative position of slit, lens, and film drum, and the significance of the flame photograph can be seen from the diagrammatic sketch of the apparatus (Fig. 5).

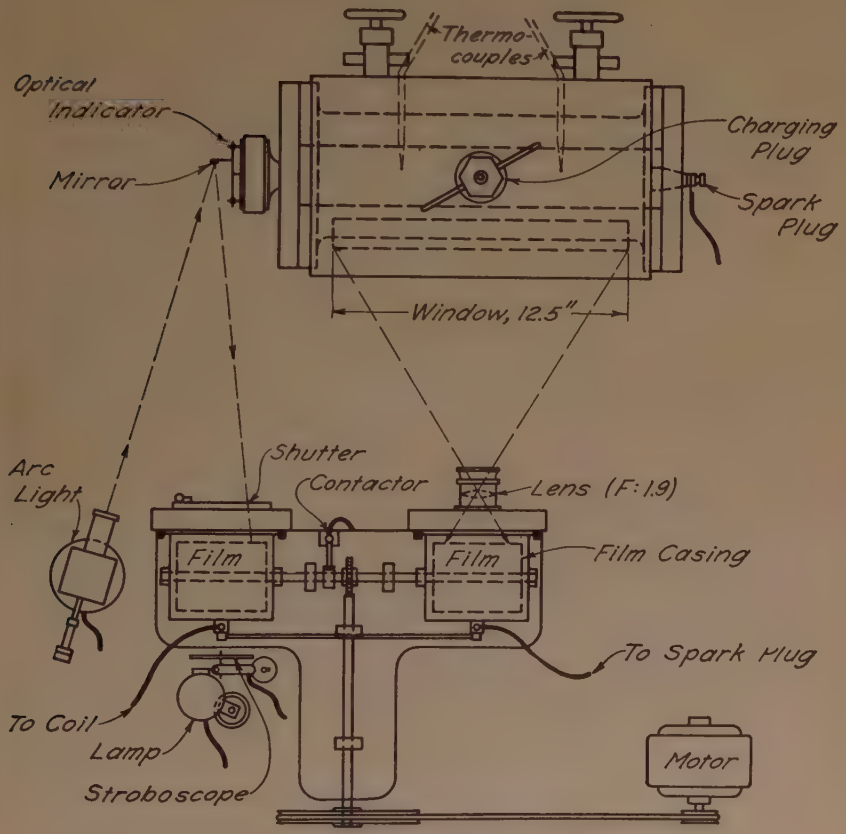


FIG. 5. DIAGRAM OF RECORDING APPARATUS

The process of photographing the flame of an explosive reaction is difficult, since the light is not of very great intensity or actinic value, and since it is of very short duration. After some experimental work with various films, Eastman Superspeed motion picture film (unperforated) was adopted. This film was rendered more sensitive to the orange and red by bathing it in a pinacyanol dye bath.* The dye bath as recommended by Walter and Davis was used.

*"Studies in Color Sensitive Photographic Plates, and Methods of Sensitizing by Bathing," F. M. Walter and R. Davis, Sci. Paper No. 422, Bureau of Standards, 1921.

Sensitizing Solution

Stock solution
- Ethyl alcohol ..... 1000 c.c.
- Pinacyanol (crystals) ..... 1 gm.

Film bath
- Distilled water ..... 60 parts
- Ethyl alcohol ..... 40 parts
- Pinacyanol stock solution ..... 4 parts
- Ammonia (28 per cent) ..... 2 parts

The films, after being cut to the proper length, were bathed in this solution for 5 minutes (bath at room temperature). They were then washed for 2 minutes in ethyl alcohol, and dried as rapidly as possible, in a current of air. All these operations were, of course, carried out in total darkness.

The films thus prepared were exposed as soon as possible after bathing, to minimize the fogging effects of the sensitizing bath.

The developer used was glycin, which was selected on account of its non-fogging qualities when used for developing under-exposed films (as most of those taken were). The developer solution was prepared according to the directions of the maker of the glycin (Hauff).

Films supersensitized and developed in this manner gave good negative images of the flame of the explosion. In some cases it was possible to dispense with the supersensitizing bath, owing to the greater intensity and actinic value of the light emitted when certain mixtures were exploded.

20. *Ignition Apparatus.*—The charge of fuel and air in the bomb was ignited at the end of the bomb opposite the indicator connection, as shown in Fig. 5. Ignition was effected by a high tension spark, controlled by a timer on the shaft driving the film drums. The spark gaps on the film drums were connected in series with the gap in the bomb, so that the passage of the spark across the three gaps was, for the purposes of this investigation, practically simultaneous.

The spark gaps in the explosion bomb were of two types. The first was the ordinary type of single gap spark plug, so arranged that the spark occurred at the center of the end of the bomb and flush with the inner surface of the head of the bomb. The second type was a multiple gap, consisting of seven gaps, each of 0.02 inch, arranged as shown in Fig. 6. By the use of this gap the combustion was initiated as practically a plane wave, so that disturbing effects, such as those due to reflected waves from the sides of the bomb, which may occur when single central ignition is used, were eliminated. The plate on which the multiple gap

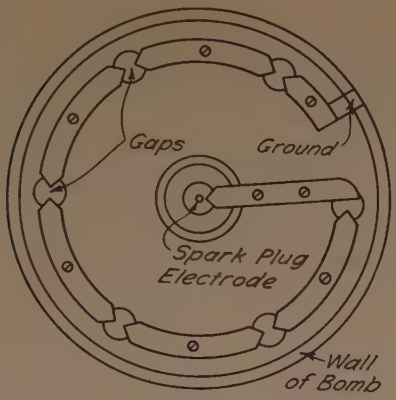


FIG. 6. MULTIPLE GAP IGNITOR

was mounted was set ½ inch from the end of the bomb, and thus the effective length of the bomb was reduced to 22.0 inches when this type of gap was used.

21. *Timing Apparatus.*—For the purposes of this investigation an accurate measurement of the time scale of the records obtained was essential. The timing apparatus consisted of a sectored disc or stroboscope driven by a small synchronous motor, which was controlled by an electrically driven tuning fork. The tuning fork had a frequency of 50 vibrations per second. An incandescent lamp of high intensity was placed so that its rays fell on a pinhole in the indicator film drum casing, the rays being interrupted, however, by the sectored disc of the stroboscope (Fig. 5). The slots in the disc were so arranged that the light was allowed to pass through and produce a dot on the moving film at intervals of 0.1 second. In this way a very accurate and convenient time scale was obtained on the indicator film. Since the two film drums were of the same diameter and were coupled to the same shaft, it is evident that the same time scale applied to both records.

22. *Temperature and Pressure Measurement.*—Initial temperatures were measured by copper-constantan thermocouples inserted in the bomb as shown in Fig. 5. One couple was also placed in the extension cylinder. The e.m.f. given by the couples was determined by means of a Leeds and Northrup precision potentiometer, and readings of the temperature of the gas in the bomb were made immediately before and after each explosion.

Initial pressures were measured by means of a test gage of the Bourdon type, connected to the bomb by one of the needle valves. This gage was calibrated, and the proper corrections were applied to its readings.

23. *Fuel Measurement and Charging.*—The fuel was enclosed and sealed in small glass capsules. The net weight of the fuel in each capsule was determined by means of a chemical balance, the weighing being carried out to 0.1 milligram.

A heavy steel plug (Fig. 5) afforded an opening through which the fuel was charged into the bomb. The glass capsule was fastened to a rod running axially through the plug. The plug was then screwed into place, and by striking the end of the rod a sharp blow, the glass capsule was driven against the lower wall of the bomb and broken.* The method described above insured against the escape of any of the volatile fuel by evaporation or leakage.

V. Method of Conducting Experiments

24. *Procedure in Making an Explosion.*—Before charging the fuel into the explosion bomb, the apparatus was heated to the desired temperature by means of the electrical heating coil. Since the gas in the bomb was entirely surrounded by the hot walls and since it was not in motion, it was considered that the temperature indicated by the thermocouples in the bomb was that of the air and fuel mixture.

When the desired temperature was reached an adjustment of the heating current was made, in order to maintain the temperature constant. The valves of the bomb were then closed, the fuel capsule was inserted into the holder, and the charging plug (Fig. 5) was screwed into place, closing the bomb. A sharp blow on the upper end of the capsule holder broke the fuel capsule against the bottom of the bomb, liberating the ether. Air was then admitted through one of the needle valves until the desired initial pressure was obtained. All valves were then closed, and the gases in the bomb were allowed to stand to permit thorough diffusion. The period of time allowed for diffusion was 15 minutes or more. For a bomb of the small size used, and with the additional effect of turbulence caused by the admission of high pressure air, it is probable that a thorough mixture was attained in the time allowed.

After loading the film drums and setting them in place on the apparatus, the timing disc (stroboscope) was started, the film drums were rotated, and an initial pressure line was taken on the indicator

*The broken glass was cleaned out of the cylinder after every three or four tests. At the same time the glass window was cleaned on the inside.

film drum by opening the shutter (Fig. 5) during one revolution of the drum. The shutter on the flame photograph film drum was opened, and the charge was fired by closing the firing switch, which allowed the timer on the film drum shaft to complete the primary circuit of the ignition system. The closing of the firing switch also illuminated the lamp behind the sectored disc, and in this way the time record was secured. After ignition, the drums were allowed to rotate one complete revolution with all the shutters open. The shutters were then closed. The exhaust valve (Fig. 5) was opened, and the pressure in the bomb was reduced to atmospheric pressure. An atmospheric or zero pressure line was then taken on the indicator film drum by opening the shutter for one complete revolution of the drum.

After stopping the apparatus, the film drums were removed and the films developed. The temperature of the gases in the bomb was determined immediately before and after each explosion. The temperature given in Table 3 (page 37) as the initial temperature is the mean of the readings before and after making the explosion. These two readings seldom differed by more than two or three degrees.

25. *Calculation of Air:Fuel Ratio.*—After charging the fuel into the bomb, the latter contained a known weight of ethyl ether, together with a mass of air at a known pressure, temperature, and volume. Since the volume, weight, and temperature of the ether vapor were also known, the partial pressure of the ether vapor could be calculated from the characteristic equation for ether vapor. For the purposes of this investigation, since more accurate data are not available, ether was assumed to follow the perfect gas law

$$PV = MBT$$

Denoting by the subscript f all quantities relating to the ether vapor and by the subscript a all quantities relating to the air, the partial pressure of the ether vapor is

$$P_f = \frac{M_f B_f T}{V}$$

The partial pressure of the air is then

$$P_a = P - P_f = P - \frac{M_f B_f T}{V} \tag{30}$$

where P is the total absolute pressure. The weight of air is

$$\mathrm{M}_a = \frac{P_a V}{B_a T} = \frac{PV - M_f B_f T}{B_a T} \tag{31}$$

The ratio of air to fuel, by weight, is then

$$R = \frac{M_a}{M_f} = \frac{P\,V}{M_f\,B_a\,T} - \frac{B_f}{B_a} \qquad (32)$$

where V = volume of bomb, cu. ft.; T = temperature, deg. F. abs.; P = pressure, lb. per sq. in. abs.; M_f = weight of fuel, lb. The value* of B for ethyl ether is $\frac{1544}{\text{molecular weight}}$

or 20.84. The value of B for air is 53.34. Then

$$\frac{B_f}{B_a} = \frac{20.84}{53.34} = 0.39$$

For the 15-inch bomb the total volume is 197.27 cu. in. or 0.11464 cu. ft. Since all the quantities of the right-hand member of equation (32) are known, the air:fuel ratio R can be calculated.

The equation representing the complete combustion of ethyl ether is

$$C_2H_5OC_2H_5 + 6O_2 = 4CO_2 + 5\,H_2O$$

The weight of air required to burn one unit weight of ethyl ether is calculated from this equation and is found to be 12.38. Then the percentage of the theoretical air used in an explosion performed with an air:fuel ratio R is $\frac{R}{12.38}$.

26. *Computation and Plotting of Pressure Curve.*—The distances on the indicator and flame films from the point opposite the auxiliary spark gaps (Fig. 6) to the point opposite the indicator mirror or lens, respectively, were determined by measurements of special photographs made with the film drums stationary. By laying off the distances thus determined on the films, a point on each record was found corresponding to the time at which ignition occurred in the bomb. The points thus determined were taken as the zero of the time record.

By measuring the distance between the dots made on the indicator film by the stroboscope lamp, the time scale of the films was established.

The ordinates of the pressure curve as recorded on the film were measured from the atmospheric pressure line and the abscissas were measured from the zero time point. The measurements were made by

*Goodenough, G. A., "Principles of Thermodynamics," p. 35.

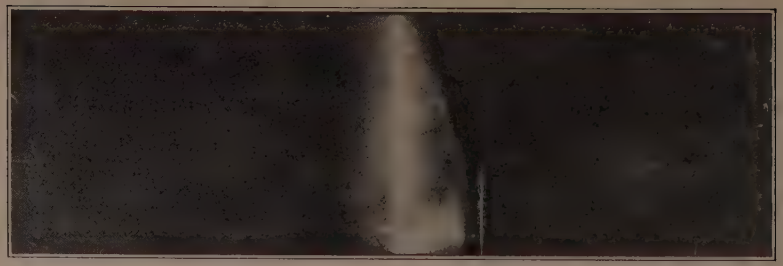


Fig. 7. Flame Photograph for Test No. 4

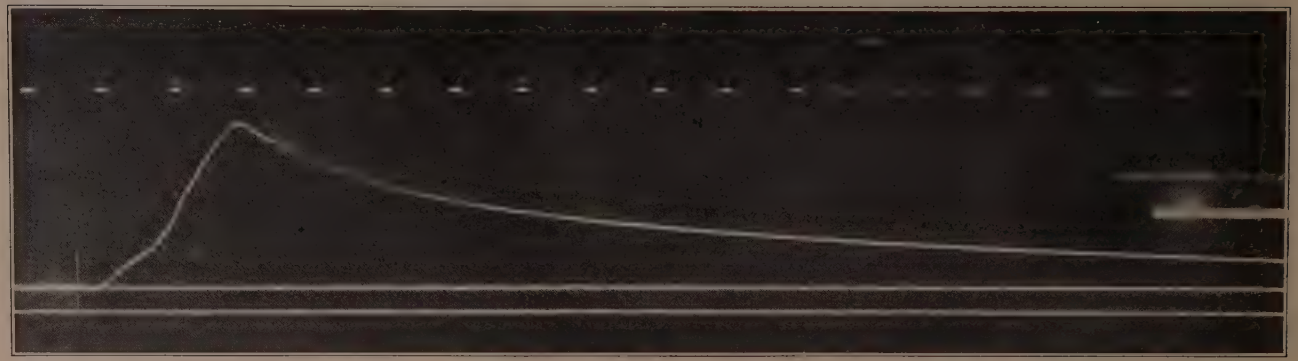


Fig. 8. Indicator Diagram for Test No. 11

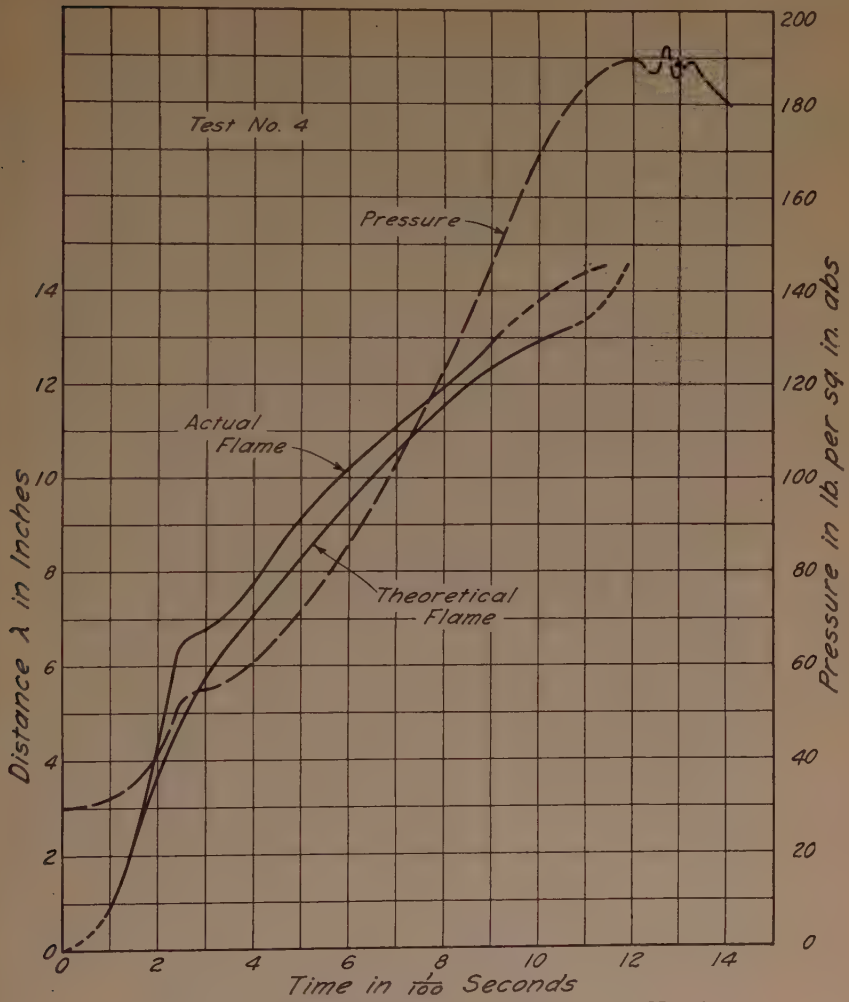


FIG. 9. PRESSURE AND FLAME CURVES FOR TEST NO. 4

means of a micrometer microscope reading to 0.1 mm. The data obtained were converted to pressures in lb. per sq. in. abs., and time in seconds, and were plotted as, for example, in Fig. 9.

27. *Computation and Plotting of Flame Curve.*—The ordinates of the flame photograph (Fig. 7) represent time (along the length of the film) and the abscissas represent distance of flame travel (across the width of the film). The flame photographs were measured to 0.1 mm. by means of the micrometer microscope. The same time scale was applied as in the case of the indicator film.

The coördinate representing flame travel was determined from the equation

$$\lambda_0 = 12.5 \frac{x}{L} + a$$

in which

λ_0 = actual flame travel, inches.
x = distance to a given point on the photograph, mm.
L = total width of photograph, mm.
a = distance from end of window to ignition point.

The length of the window was 12.5 inches; a, the distance from the end of the window to the ignition point, was 1.0 inch, 1.5 inch, or 8.5 inches, depending on the size of the bomb and the type of ignition used.

The flame travel, as previously determined, was then plotted against the time in seconds (Fig. 9).

28. *Precision and Accuracy of Measurements.*—

(a) Temperature Measurements

The temperature measurements, made by means of the thermocouples and precision potentiometer, were correct and accurate to 1 deg. F. The couples were calibrated against a certified thermometer.

(b) Fuel Weight

The ethyl ether used as fuel was weighed to 0.1 milligram.

(c) Initial Pressure

The gage used for measurement of initial pressure was graduated to 1 lb. per sq. in., and from calibration it was determined that the gage was accurate to 0.5 lb. per sq. in.

(d) Explosion Pressure

The indicator diagram could be read with a precision corresponding to 1 lb. per sq. in. As stated in Section 16 it was determined that the instrument was able to follow the most rapid variation of pressure which would be likely to occur in such explosions as were being investigated.

(e) Flame Propagation

The flame photographs were in most cases quite distinct, and could be measured to 0.2 mm. easily. Since the width of the photograph was about 32 mm., representing an actual flame travel of 12.5 inches, the possible error of 0.2 mm. in measurement represents only about 0.08 inch in actual flame travel.

VI. Results

29. *Comparison of Actual and Calculated Flame Curves.*—In Fig. 7 is shown the flame photograph of an explosion made under the following conditions:

Test No. 4

Length of bomb, 14.5 inches. Multiple gap ignition.
Initial pressure, 30.9 lb. per sq. in. abs.
Initial temperature, 199 deg. F.
Air:Fuel ratio, 10.49. Per cent of theoretical air, 84.8. Figure 9 shows the pressure and flame propagation curves, as computed from measurements of the indicator diagram and flame photograph.

Table 2 gives the calculations of the theoretical analysis for Test No. 4. For the particular test under consideration (Test No. 4) the various preliminary values are calculated as follows:

(a) Temperature resulting from adiabatic combustion

Initial Mixture

$C_2H_5OC_2H_5$	1.000 lb.	1.000 mols
O_2	2.184	5.060
N_2	8.306	22.000
Total	11.490 lb.	28.060 mols

Calculating* the maximum temperature due to the adiabatic combustion, it is found to be 5010 deg. F. abs. The corresponding maximum pressure is 259.5 lb. per sq. in. abs. The value of Π_v is then $\frac{259.5}{30.9} = 8.40$.

(b) Specific heat of the products of combustion

The products of the combustion, as existing at the maximum temperature, together with their specific heats, are

	m	γ_v''	$m\gamma_v''$
CO_2	2.36 mols	7.51	17.78
CO	1.632	4.89	7.98
H_2O	4.605	6.35	29 24
H_2	0.395	3.57	1.41
N_2	22.000	4.89	107.58
	31.000 mols		163.99

*Univ. of Ill. Eng. Exp. Sta. Bul. 139, 1923.

The specific heats of the products listed are given for a temperature of 212 deg. F. The specific heat of the products is then

$$\gamma_v'' = \frac{163.99}{31.00} = 5.29$$

(c) Specific heat of initial mixture

In the same way the specific heat of the initial mixture is found to be

$$\gamma_v' = 5.85$$

(d) Ratio of specific heats

The ratio of the specific heats of products and initial mixture is

$$\gamma = \frac{\gamma_v''}{\gamma_v'} = 0.905$$

$$(1 - \gamma) = 0.095$$

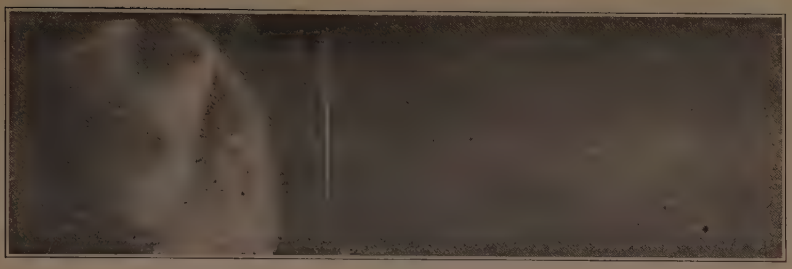
(e) Value of k

The value of k, or the ratio of the specific heats at constant pressure and constant volume, for the initial mixture, is

$$\frac{k = 10.49 \times 1.40 + 1.00 \times 1.10}{11.49} = 1.373$$

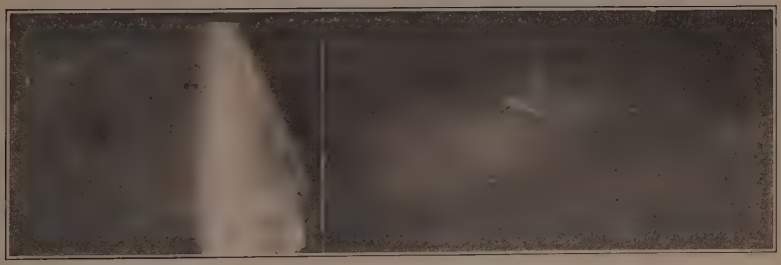
From the values of λ in Table 2 the theoretical flame curve of Fig. 9 is plotted. It is evident that the theoretical curve follows the actual curve of flame progress quite closely except in the region of the flame arrest, at 0.025 second from ignition. The theoretical analysis, of course, takes no account of such a phenomenon, and consequently the calculated flame curve shows only a slight irregularity at the point in question. The irregularity which does occur has its origin in the corresponding irregularity in the pressure curve at 0.025 second.

Figures 11, 12 and 13 show other flame curves, both theoretical and actual, with the corresponding pressure curves. The conditions under which each test was made are given in Table 3. It should be noted that in most cases the theoretical curve falls slightly below the actual curve. This difference is consistent with the fact that equation (15) takes no account of heat loss. It is evident that if heat is lost from the unburned gas before it is compressed, the exponent n of the compression PV^n = constant will be less than k, which equals 1.37, approximately. If n is less than k, as is required by the assumption of heat loss, then $(1 - \lambda)$ as calculated from equation (15) will be smaller than if n were equal to k. Thus λ would be larger, at any given time during the explosion. This is, in fact, the case, as is evident from the majority of the records obtained.



Test No. 2

Test No. 3



Test No. 8

Test No. 10

FIG. 10. FLAME PHOTOGRAPHS

TABLE 2. CALCULATIONS OF THEORETICAL ANALYSIS OF FLAME PROPAGATION

	CALCULATION OF λ										
1	Time from Ignition, ($\frac{1}{100}$ Seconds)	2	3	4	5	6	7	8	9	10	11
2	P, (lb. per sq. in. abs.)	42.0	53.5	60.6	71.7	86.5	103.8	124.0	146.5	168.8	184.
3	Π	1.36	1.73	1.96	2.32	2.80	3.36	4.01	4.74	5.46	5.95
4	$\Pi_v - \Pi$	7.04	6.67	6.44	6.08	5.60	5.04	4.39	3.66	2.94	2.45
5	$\Pi^{\frac{1}{1.37}}$	1.25	1.49	1.63	1.85	2.12	2.42	2.75	3.11	3.45	3.67
6	$\Pi^{\frac{1}{1.37}}(\Pi_v - 0.905) - 0.095\Pi$	9.23	11.00	12.02	13.63	15.60	17.80	20.22	22.85	25.32	26.93
7	$1-\lambda$	0.763	0.606	0.536	0.446	0.359	0.284	0.217	0.160	0.116	0.091
8	λ	0.237	0.394	0.464	0.554	0.641	0.716	0.783	0.840	0.884	0.909
9	λl, (Inches from Ignition Point)	3.43	4.26	6.73	8.04	9.30	10.38	11.35	12.18	12.82	13.18
	VALUES OF λ MEASURED FROM PHOTOGRAPH										
10	$\lambda_o l$	4.30	6.72	7.74	9.08	10.24	11.00	11.88	12.85		
11	λ_o	0.297	0.464	0.534	0.626	0.704	0.758	0.819	0.887		
12	$1-\lambda_o$	0.703	0.536	0.466	0.374	0.296	0.242	0.181	0.113		
13	$(1-\lambda_o)l$	10.20	7.78	6.76	5.42	4.26	3.50	2.62	1.05		
	CALCULATION OF n										
14	Log Π	0.134	0.238	0.292	0.366	0.447	0.526	0.603	0.676		
15	$\Pi_v - \Pi$	7.04	6.67	6.44	6.08	5.60	5.04	4.39	3.66		
16	$(\Pi_v - 0.905)(1-\lambda_o)$	5.27	4.02	3.49	2.80	2.22	1.81	1.36	0.846		
17	$\frac{\Pi_v - \Pi}{(\Pi_v - 0.905)(1-\lambda_o)}$	1.336	1.660	1.844	2.170	2.527	2.780	3.238	4.320		
18	$\frac{0.095\,\Pi}{\Pi_v - 0.905}$	0.017	0.022	0.025	0.029	0.036	0.043	0.051	0.060		
19	Sum (17) + (18)	1.353	1.682	1.869	2.199	2.563	2.823	3.289	4.380		
20	Log (19)	0.131	0.226	0.272	0.342	0.409	0.451	0.517	0.642		
21	n = (14) ÷ (20)	1.02	1.06	1.08	1.07	1.09	1.17	1.17	1.05		
	CALCULATION OF m										
22	$\Pi_v \div \Pi$	6.17	4.85	4.29	3.62	3.00	2.50	2.09	1.77		
23	Log $(\Pi_v \div \Pi)$	0.790	0.666	0.632	0.559	0.477	0.398	0.320	0.250		
24	$\Pi^{\frac{n}{n}}$	1.35	1.68	1.87	2.20	2.56	2.82	3.29	4.38		
25	$\Pi^{\frac{n}{n}}(1-\lambda_o)$, (24) x (12)	0.950	0.900	0.872	0.823	0.758	0.682	0.595	0.435		
26	1 - (25)	0.050	0.100	0.128	0.177	0.242	0.318	0.405	0.505		
27	λ_o	0.297	0.464	0.534	0.626	0.704	0.758	0.819	0.887		
28	(27) ÷ (26)	5.94	4.64	4.17	3.54	2.91	2.38	2.02	1.75		
29	Log (28)	0.774	0.667	0.620	0.549	0.464	0.377	0.305	0.243		
30	m, = (23) ÷ (29)	1.02	1.03	1.02	1.02	1.03	1.06	1.05	1.03		
	CALCULATION OF ψ_{ch}										
31	$(\Pi_v \div \Pi) - 1$, = (22) - 1	5.17	3.85	3.29	2.62	2.00	1.50	1.09	0.77		
32	$n \div [(\Pi_v \div \Pi) - 1]$ = (21) ÷ (31)	0.197	0.274	0.328	0.408	0.547	0.778	1.07	1.37		
33	1 + (32)	1.197	1.274	1.328	1.408	1.547	1.778	2.07	2.37		
34	Reciprocal of (33)	0.836	0.785	0.753	0.710	0.647	0.563	0.483	0.423		
35	$1 - (34) = \frac{\psi_{ch}}{\psi_a}$	0.164	0.215	0.247	0.290	0.353	0.437	0.517	0.577		

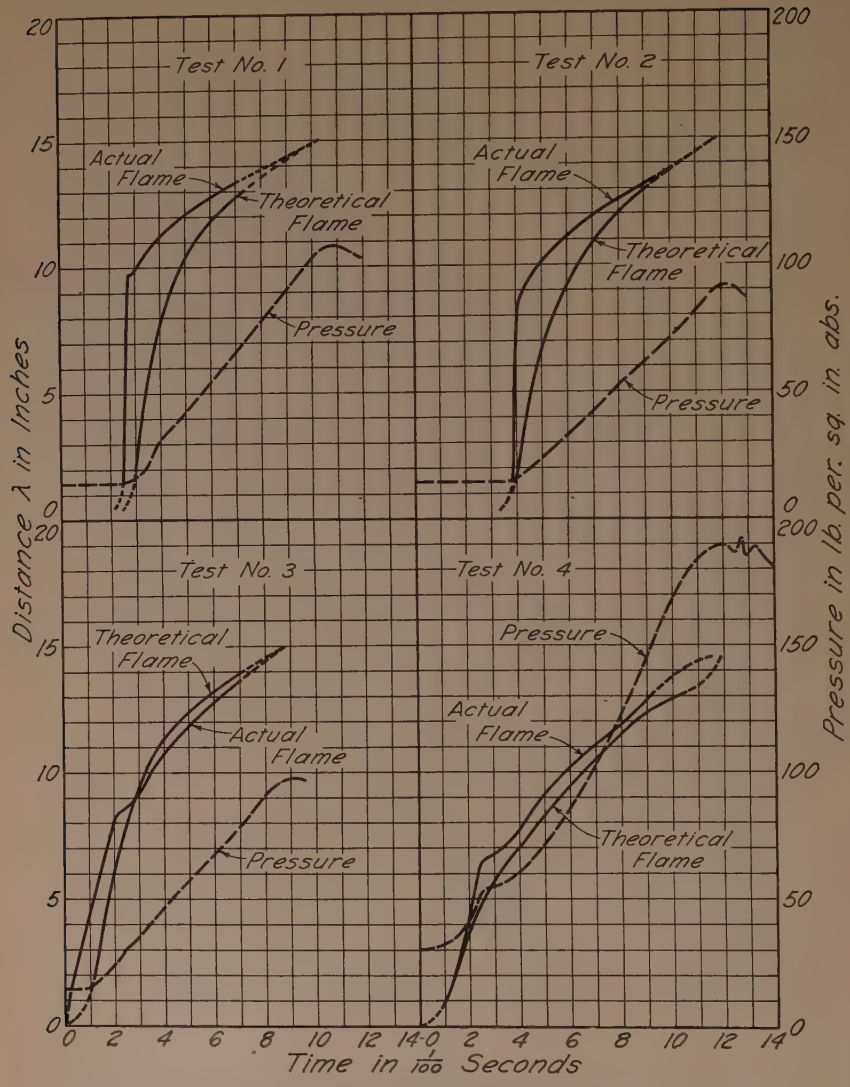


Fig. 11. Pressure and Flame Curves for Tests Nos. 1, 2, 3, and 4

It sometimes happens, however, that in the earlier stages of explosion the theoretical curves fall slightly above the actual flame curve. This can be explained by the fact that the phenomenon of flame arrest occurs in the early stages of explosion.

In the case of explosions where ignition was accomplished by a single spark at the center of one end of the cylindrical bomb, it is evident

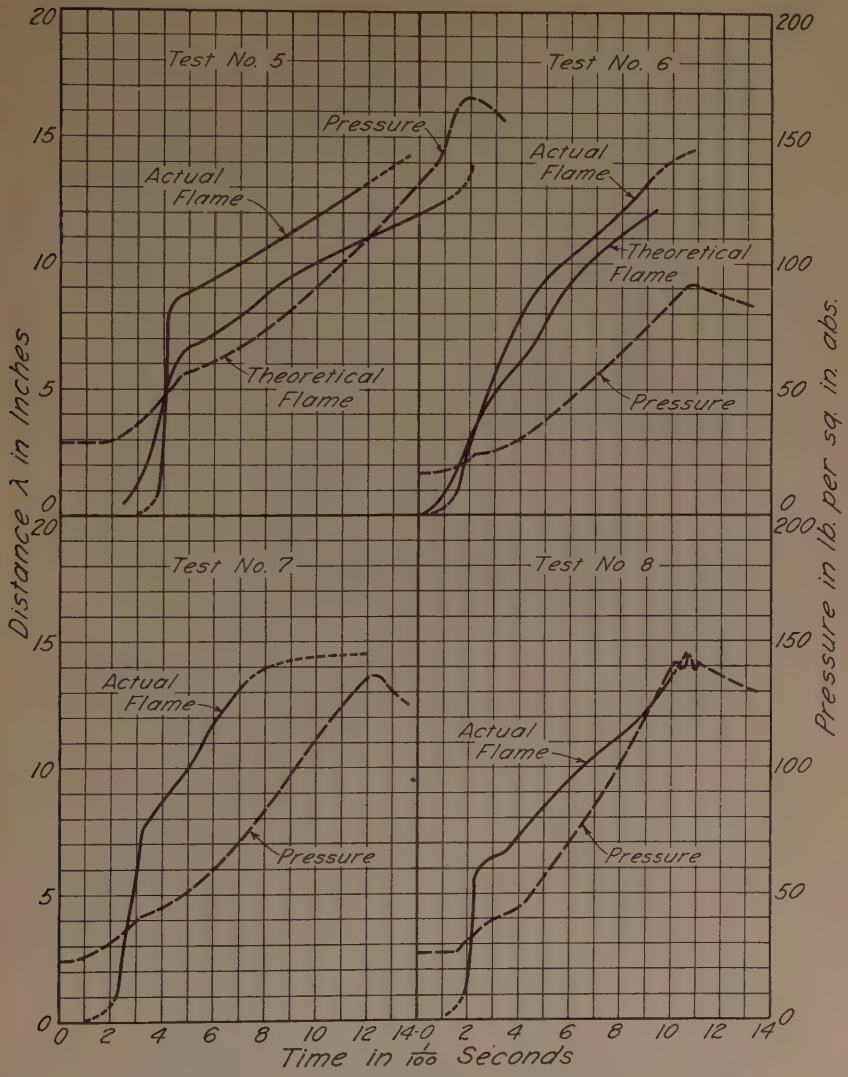


FIG. 12. PRESSURE AND FLAME CURVES FOR TESTS NOS. 5, 6, 7, AND 8

that the combustion would proceed by hemispherical waves from the ignition point, and that a flame photograph would not give a true representation of the progress of the flame, since such a photograph is not a true representation of anything except a plane wave. However, with ignition by the multiple gap, with seven sparks occurring simultaneously over quite a large proportion of the area of the cylinder, it is

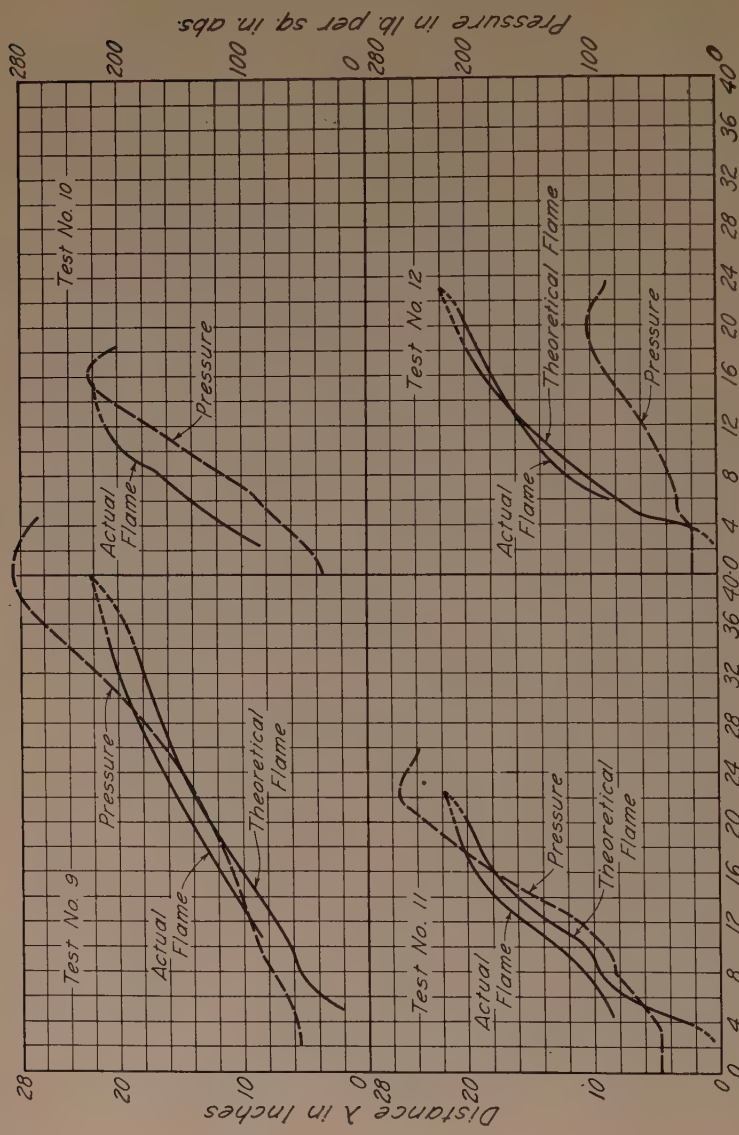


FIG. 13. PRESSURE AND FLAME CURVES FOR TESTS NOS. 9, 10, 11, AND 12

very probable that the flame front, being composed of seven small hemispherical waves and their interference waves, is substantially a plane wave.

A comparison of the flame photographs and the indicator diagrams reveals the fact that the maximum pressure developed by the explosion, in most cases, occurs at the time when the flame has com-

TABLE 3.—TEST DATA

Test No.	Air: Fuel Ratio	Per cent Theoretical Air	Initial Conditions		Length of Bomb inches	Type of Ignition	Maximum Pressure		Adiabatic Maximum Pressure	
			Temperature deg. F.	Pressure lb. per sq. in. abs.			lb. per sq. in. abs.	Π_{max}	lb. per sq. in. abs.	Π_v
1	7.76	62.7	124	14.4	15.0	S	107.4	7.46		
2	7.50	60.6	162	14.3	15.0	S	91.3	6.38		
3	8.89	71.8	129	14.2	15.0	S	97.2	6.85	101.5	7.16
4	10.49	84.8	199	30.9	14.5	M	188.4	6.10	259.5	8.40
5	11.57	93.5	200	28.9	14.5	M	169.9	5.88	260.5	9.03
6	10.36	83.8	189	66.9	14.5	M	362.4	5.42	554.8	8.29
7	11.29	91.2	180	24.4	14.5	M	136.4	5.59		
8	10.92	88.3	199	26.9	14.5	M	140.4	5.22		
9	13.70	110.7	213	54.4	22.0	M	283.2	5.21	419.5	7.74
10	10.61	85.7	204	35.4	22.0	M	221.4	6.25		
11	13 73	111.0	196	45.4	22.0	M	253.9	5.59	318.0	7.01
12	11.29	91.2	182	19.4	22.0	M	102.4	5.28	134.0	6.74

pletely traversed the whole volume of the bomb. The data of Woodbury, Lewis, and Canby* show that the flame of explosive mixtures completely fills the bomb at the instant of maximum pressure. The results shown here confirm, in most cases, the conclusions of Woodbury, Lewis, and Canby. However, it is evident from the curves of Figs. 11 to 13 that in some cases the maximum pressure occurs after the bomb has been completely traversed by the flame.

The analysis of flame propagation as proposed by Nägel† and as applied to actual test results is evidently a reasonably close representation of the mechanism of the normal explosive reaction in a gaseous mixture. The similarity of the calculated flame curves to the corresponding curves plotted from actual flame photographs indicates that the analysis has given a true representation of the general process, even though the introduction of the heat loss in the actual case does invalidate the equality expressed by equation (1).

30. *Velocity of Flame Propagation.*—The velocity of flame propagation varies considerably during the progress of an explosion, as is evident from an inspection of the curves derived from the flame photographs (Figs. 11 to 13). However, a general idea of the magnitude of the flame velocity can be obtained by determining the maximum velocity and the average velocity. The maximum velocity is in every case calculated from the slope of the flame curve at the time before the occurrence of the flame arrest. The average velocity is obtained by dividing

*Jour. S. A. E., vol. 8, p. 210, 1921.
†*Loc. cit.*

TABLE 4.

FLAME VELOCITIES

Test No.	Flame Velocities, ft. per sec.	
	Average	Maximum*
1	12.1	.....
2	10.1	.....
3	13.6	.....
4	10.3	34.7
5	7.7	145.8
6	11.3	25.0
7	10.1	55.6
8	12.1	111.0
9	4.6	.....
10	11.5	.....
11	8.3	.....
12	9.2	.....

*In some of the tests there was no well defined maximum velocity, and therefore its measurement was omitted in these cases.

the length of the bomb by the time elapsing from ignition to the attainment of maximum pressure. The average and maximum velocities are given in Table 4.

It should be noted that neither the maximum nor the average flame velocities show any definite dependence on initial pressure or temperature. The data of Woodbury, Lewis, and Canby* also serve to substantiate this conclusion.

31. *Flame Arrest.*—The phenomenon of flame arrest, as shown in the results of Woodbury, Lewis, and Canby,† is also present in all of the results obtained in this investigation. It should be noted that the abrupt change in velocity, as shown by the change in slope of the flame photograph curve, coincides with the time of the change of the rate of rise of pressure, as shown by the indicator diagram. According to Woodbury, Lewis, and Canby, at the time of the flame arrest the flame had progressed through about two-thirds of the length of the bomb, while only about one-fourth of the total pressure had been developed. By reference to Fig. 9 it is evident that for this particular case the flame had traveled about 6.5 inches at the instant of flame arrest, or about 43 per cent of the length of the bomb. The change in the rate of the rise of the pressure occurred at the same time, and the pressure had at this time risen to about 54 lb. per sq. in. abs., or about 29 per cent of the maximum pressure developed. Table 5 gives the distance traveled by the flame, pressure developed, and time, at the instant of the flame arrest, for the various explosions made.

*Loc. cit.
†Loc. cit.

TABLE 5.

FLAME ARREST DATA

Test No.	Distance Traveled by Flame to Point of Arrest		Pressure Developed at Point of Arrest		Time from Ignition to Flame Arrest
	Inches	Per cent	lb. per sq. in. abs.	Per cent of maximum	1/100 sec.
1	9.7	65	32	30	2.7
2	8.3	55	..	..	4.0
3	8.3	55	30	31	2.2
4	6.5	45	54	29	2.5
5	8.4	56	56	35	4.5
6	...	..	98	27	2.3
7	7.6	52	41	30	3.2
8	...	..	54	19	9.0
9	...	..	80	28	8.0
10	...	..	..	..	...
11	...	..	82	32	8.0
12	...	..	29	15	4.4

NOTE: In the tests conducted with the extension cylinder, the flame arrest occurred too early in the explosion to be photographed. Hence, no distance traveled by the flame to the point of arrest could be measured.

Tests 1, 2, and 3 were made with ignition by means of a single spark at the center of one end of the bomb, while the rest of the tests were made with ignition by means of the multiple gap. A possible hypothesis was that the flame arrest phenomenon might be attributed to the fact that with single spark ignition, the combustion proceeds in spherical waves, with centers at the spark gap. The spherical combustion zones, accompanied as they are by similarly spherical pressure waves, might possibly give rise to resonance, or similar effects, which would cause a region of very high pressure at some particular point in the bomb. The flame, upon reaching this high pressure zone, would then be abruptly checked, and the flame arrest would appear in the photographs. If this hypothesis is correct, the flame arrest would probably not appear in tests made with ignition by means of the multiple gap. The multiple gap starts seven small spherical waves, which undoubtedly soon merge into a wave front which is practically a plane, and which would not give rise to any resonance phenomena or reflected waves from the side walls of the bomb. However, it is evident from the photographs (Fig. 10) and the curves of flame propagation (Figs. 11 to 13) that the flame arrest *does* exist, irrespective of which of the two types of ignition was used. It is very probable, then that the cause of the flame arrest must be sought elsewhere.

Dixon* states that the flame arrest occurring in explosions in closed tubes is due to a wave which travels with the velocity of sound from the ignition point to the opposite end of the tube, and, rebounding from the end, strikes the advancing flame front, producing the arrest. Dixon's work,† however, was done with detonating mixtures, and the velocities of flame travel attained were much greater than in the tests discussed here. It is entirely possible, then, that the cause of the flame arrest found by Dixon was the reflected wave. An approximate calculation of the velocity and the distance traveled by such a wave can be made, using data taken from the tests discussed here.

Approximate velocity of sound.....1120 ft. per sec.
Time elapsing (average of all tests) from ignition to flame arrest .....0.045 sec.
Distance traveled by a sound wave in 0.045 sec. = 50 ft. approximately.

It is evident that the reflected wave originating at the instant of ignition could not cause the flame arrest, since, in the time during which the flame advanced to the point of arrest, the wave would have traveled about 40 times the length of the bomb.

The results of Woodbury, Lewis, and Canby show that when turbulence is produced by a rapidly rotating fan, the flame arrest still exists in practically the same position. However, as the turbulence is increased, by increasing the speed of the fan, the flame arrest becomes less pronounced. These facts suggest the hypothesis that a possible cause of the flame arrest is the partial extinction of the flame on account of low density of the gas. Figure 19, a diagram of motion of various planes of gas during the explosion, shows clearly the great decrease in density of the gas behind the flame front. It is entirely possible that this region of low density extends into the combustion zone itself, and that when the density reaches a certain minimum, partial extinction of the flame occurs. The momentary cessation of the motion of the flame affords an opportunity for pressure equalization, as shown by the pressure diagram at the instant of the flame arrest, and the consequent increase in density in the combustion zone allows the flame to proceed again.

Investigations of the limits of inflammability of explosive mixtures have shown that the range of mixtures within which inflammation will take place narrows down rapidly as low densities are approached.‡

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*Jour. Chem. Soc., vol. 99, p. 594.
†Jour. S. A. E., vol. 9, p. 240, 1921.
‡Burrell, G. A. and Robertson, I. W., "Effects of Temperature and Pressure on the Explosibility of Methane-Air Mixtures," Bur. Mines Tech. Paper 121, 1916.

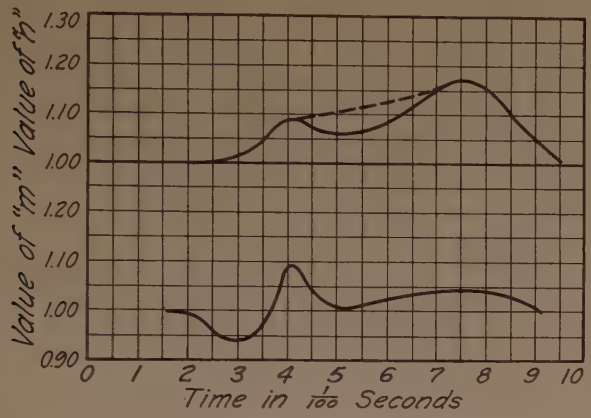

FIG. 14. CURVES OF THE VARIATION OF THE VALUES OF m AND n FOR TEST NO. 4

It is probable that the same general variation occurs with ether-air mixtures, and if so, it is entirely possible that the occurrence of low densities in the combustion zone might cause the partial extinction of the flame. This hypothesis at least does not conflict with certain facts regarding the flame arrest, which have been demonstrated by the results of Woodbury, Lewis, and Canby, and also by those of the present investigation.

32. *Character of Expansion and Compression of Gases During the Explosion Process.*—Figure 14 shows the curve for the variation of the exponent n, during the explosion process, for the unburned gas ahead of the flame front, for Test No. 4. In the equation for polytropic changes of state,

$$PV^n = \text{constant}$$

Different values of n denote various conditions existing during the compression, as follows:

$n = 1$, isothermal compression
$1 < n < k$, compression with loss of heat from the gas
$n = k$, adiabatic compression
$n > k$, compression with heat added to the gas

The curve of Fig. 14 shows that at 0.02 second after ignition the value of n is 1.00, or that the gas is being compressed isothermally. This fact is consistent with the usual conception of the mechanism of explosions since it is very probable that the unburned gas loses heat rapidly at first, and since the mass of gas being compressed is so large during the early

stages of combustion that the initial compression in any case would appear almost isothermal. As the combustion proceeds, the value of n becomes greater, reaching 1.09 at 0.04 second, shortly after the occurrence of the flame arrest. The increase in the value of n shows that the compression is becoming more nearly adiabatic than isothermal, which is explained by the fact that conduction and radiation from the burned gas begin to affect the unburned gas. The decrease of the value of n after 0.04 second is probably due to the flame arrest which occurred a short time previously. It is evident that a phenomenon such as the flame arrest would cause a discontinuity in the explosion process, and that any equations representing the progress of the explosion would not be valid at the time of the flame arrest. That is, it is quite possible, if the flame arrest had not occurred, that the curve showing the value of n would have continued along the path shown by the dotted line in Fig. 14, and would have joined the solid line curve at about 0.075 second after ignition. At this time the value of n is 1.17, indicating that the compression has approached more nearly to the adiabatic. After 0.075 second the value of n decreases, and near the end of the explosion process it again reaches the value 1.00, showing that heat loss from the unburned gas increases as the amount of unburned gas decreases.

Figure 15 shows other curves of the values of n, plotted with the time from ignition as abscissas. Some of these curves show a tendency upwards in the earlier stages of explosion. The flame arrest is probably the cause of this upward tendency, as the time at which the flame arrest occurs agrees with the time of the upward trend of the "n" curves. As the flame arrest exists as a discontinuity in the explosion process, it is difficult to assign any definite reason for the high values of n at the time of its occurrence. It should be noted that in all of the curves of n, except those for Tests Nos. 3 and 12, the values of n are below k, showing that heat is being lost from the unburned gas continuously during the explosion process. However, in Test No. 3 the value of n reaches 1.60, and in Test No. 12 it exceeds 2.00. Hence in these tests heat was being added to the unburned gas during its compression. It is difficult to give any reason for such an occurrence in these two particular tests, as the conditions do not differ greatly from those of other tests in which the values of n conformed more nearly to the normal.

All of the curves of n show, however, a rise in the value of n (indicating heat added or, at least, a decrease of heat loss) as the explosion proceeds towards its later stages. This net decrease of the rate of heat loss from the unburned gases is naturally due to the increased temperature of the burned gases and the consequent increase in the rate of flow of heat from the burned to the unburned gas. As discussed previ-

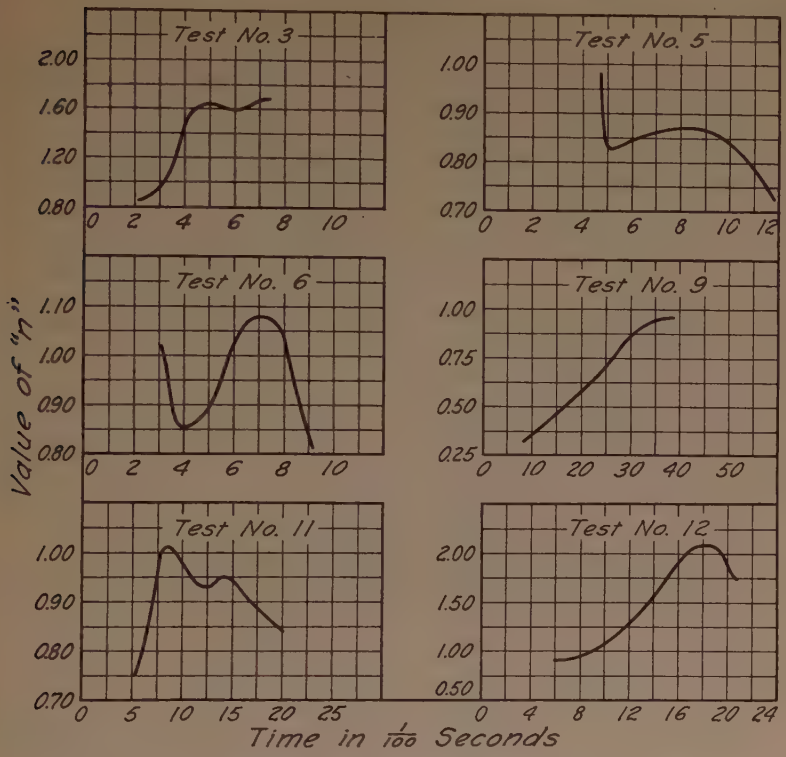

FIG. 15. CURVES OF THE VARIATION OF THE VALUE OF n FOR TESTS NOS. 3, 5, 6, 9, 11, AND 12

ously, for Test No. 4, all the curves of n show a decrease at the end of the combustion, indicating that the rate of heat loss increases as the end of the explosion is reached.

Figure 14 also shows the variation in the value of m (the exponent referring to the burned gases). It should be noted that m varies between 0.94 and 1.09, indicating that at all times during the explosion process heat is being added to the burned gas. The value of m for an adiabatic expansion would have been $k = 1.37$. It is evident then that the reaction does not confine itself strictly to the combustion zone or flame front. The evolution of heat by chemical reaction continues in the so-called "burned gas" long after the flame front has passed through any individual portion of the gas. F. W. Stevens* states that the flame phenomena do not include all of the reaction and that afterburning must exist. Furthermore, when the process of combustion is considered in the

*Jour. S. A. E., vol. 9, p. 241. 1921.

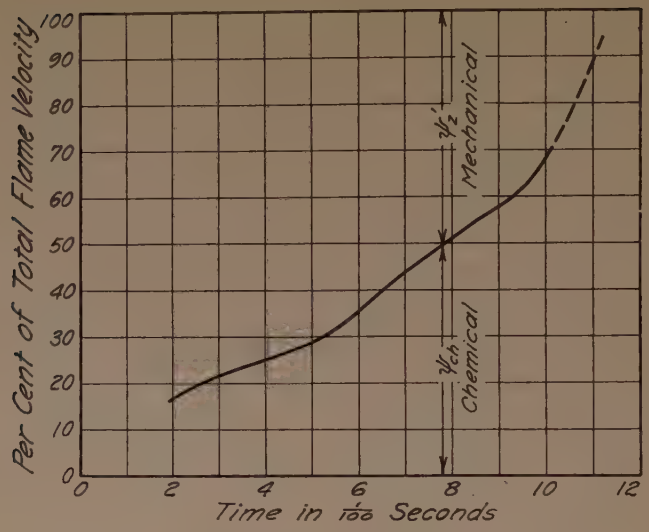

FIG. 16. CURVE SHOWING THE DIVISION OF THE TOTAL FLAME VELOCITY FOR TEST NO. 4

light of the thermodynamic theory discussed in Bulletin No. 139 of the Engineering Experiment Station, it is evident that the chemical equilibrium of the gases after the flame front has passed must alter as the pressure and temperature change. In general there is a decrease of temperature and pressure behind the flame front as the combustion progresses, and hence the chemical reaction would tend to alter towards the completion, and heat would be evolved.

The values of m are not consistent in their variation, as the factors influencing chemical equilibrium and heat flow behind the flame front vary independently. However, the values of m for all tests are without exception below k ($= 1.37$), and therefore confirm the preceding deductions relative to afterburning and adjustment of the chemical equilibrium.

33. *Reaction Velocity.*—A method was derived in Section 7 for calculating the relative amount of the total flame velocity which was due to the chemical reaction velocity only, that is, to the spread of the flame from one molecule to the next. Figure 16 shows, for Test No. 4, the division of the total velocity into forward velocity of the molecules Ψ_z' (mechanical velocity) and reaction velocity Ψ_{ch} (chemical). The chemical reaction velocity at 0.02 seconds after ignition (the earliest point of the explosion at which computations could be made) was 16 per cent

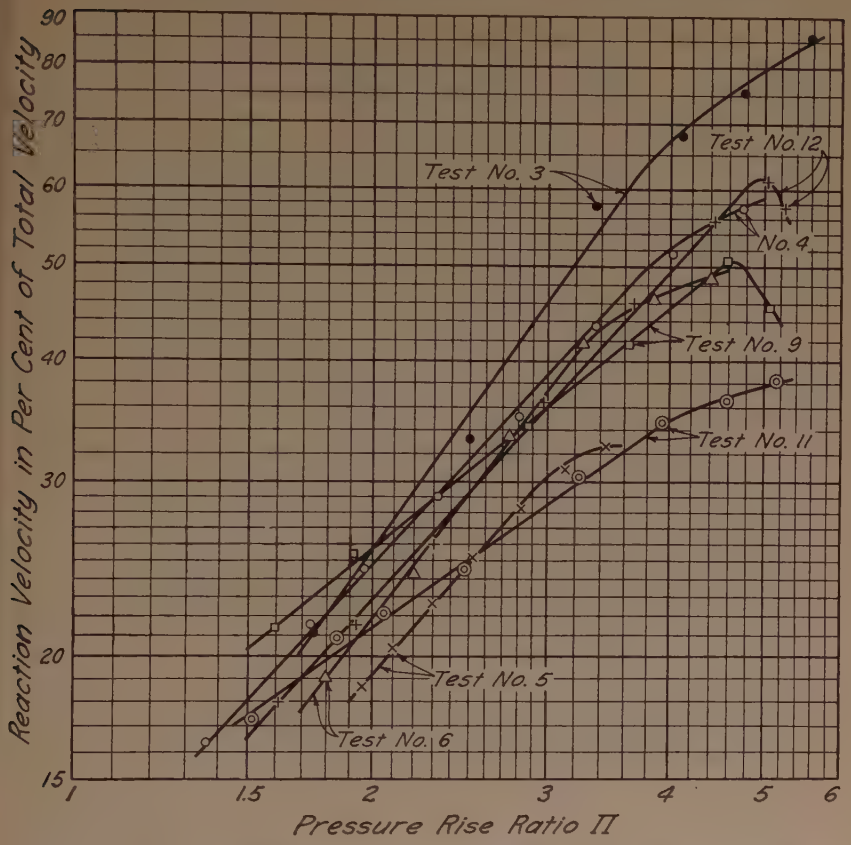

FIG. 17. CURVE SHOWING VARIATION OF REACTION VELOCITY WITH PRESSURE

of the total flame velocity. The reaction velocity then increased until at 0.10 second it was 68 per cent of the total flame velocity. The curve naturally tends upwards from the last calculated point at 0.10 seconds, and can be extended to 100 per cent at the time the flame fills the bomb. That is, at the end of the explosion process, when the end wall of the bomb is reached, the total flame velocity is entirely due to chemical reaction velocity.

Figure 17 shows the curves of the reaction velocity, expressed in per cent of the total flame velocity, plotted against the pressure rise ratio Π for Tests Nos. 3, 4, 5, 6, 9, 11, and 12. The curves are plotted using logarithmic coördinates. Only the portions of the reaction velocity curves occurring after the flame arrest have been used, since before and during the flame arrest the process is discontinuous and the

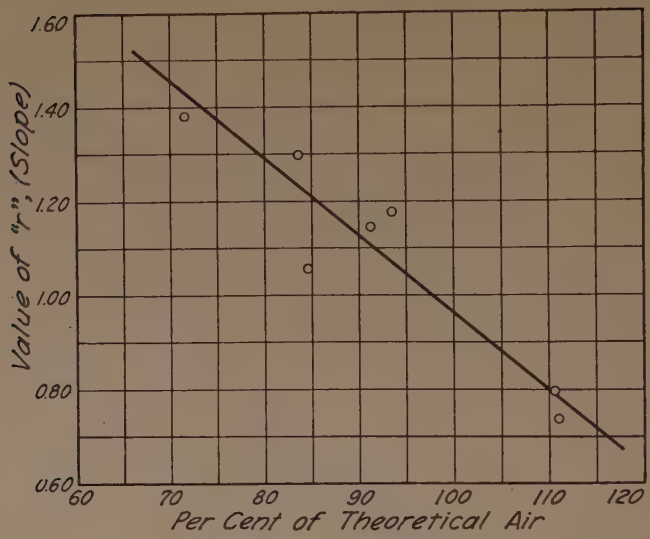

FIG. 18. CURVE SHOWING VARIATION OF SLOPE OF REACTION VELOCITY CURVES WITH FUEL MIXTURE

equations deduced in Section 7 cannot be considered as valid for a discontinuous process, such as the flame arrest.

All of the curves of reaction velocity shown in Fig. 17 are straight lines, excepting at the upper extremity. This part tends to drop. The curves all have approximately the same slope. That is, the extreme range of variation in slope, considering the straight line portions of the curves only, is from 0.72 to 1.38.

In Fig. 18 the slopes of the various reaction velocity curves shown in Fig. 17 are plotted, using as abscissas the per cent of theoretical air in the mixture exploded in each test. While the points do not all lie on a smooth curve, the decreasing trend of the slope with the leaner mixtures is very evident. The reaction velocity curves are straight lines when plotted with logarithmic coördinates, and a general equation can be deduced giving the proportion of the total flame velocity which is due to chemical reaction velocity, in terms of the pressure rise and the characteristics of the fuel mixture. Such an equation would have the form

$$V_r = \frac{\Psi_{ch}}{\Psi_z} = c\,\Pi^r$$

where Π as before, represents the pressure rise ratio. The exponent r as is evident from Fig. 18, has the form

$$r = at + b$$

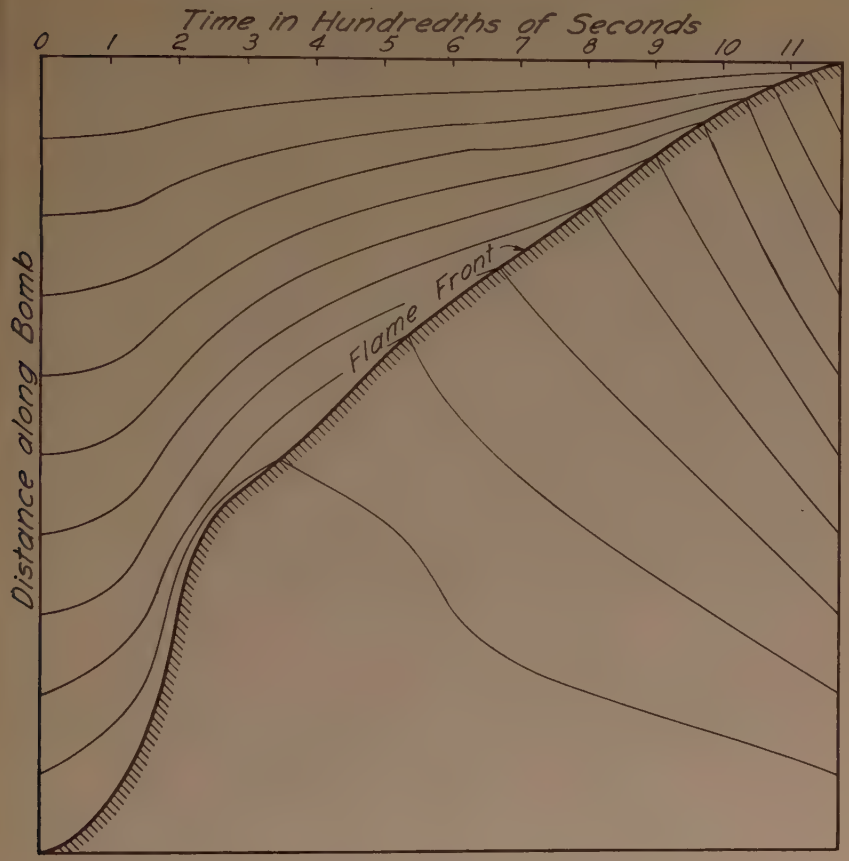

FIG. 19. GAS MOVEMENT DIAGRAM FOR TEST NO. 4

where t is the per cent of theoretical air in the initial fuel mixture. The constants a and b are determined from Fig. 18 and r becomes

$$r = 2.60 - 0.0163\,t$$

Then the reaction velocity, expressed as a fraction of the total flame velocity, is

$$V_r = c\,\Pi^{(2.60-0.0163t)}$$

This equation, of course, applies only for mixtures of ethyl ether and air, and for the mixture range specified. The dependence of the reaction velocity on the mixture strength is, in the tests considered, well defined, and is in general accord with the law of mass action.

34. *Gas Movements During Explosion.*—Midgley* has derived a method for showing the motion of the various planes of gas in a cylindrical bomb during explosion. The method was applied by him to the results of Woodbury, Lewis, and Canby, with, however, the assumption of a "typical" pressure curve and of adiabatic conditions during explosion. Figure 19 gives a diagram showing the motion of the various planes of gas during the progress of the combustion (based on the results of Test No. 4). Starting, for instance, with a plane of gas which was initially half way down the length of the bomb from the ignition point, the gas in this plane at first moves forward ahead of the flame front slowly, then increases in velocity, and finally at 0.09 second after ignition, it is overtaken by the flame front and burns. It is then thrown to the rear (towards the ignition point) with quite a high velocity and finally at the end of the combustion process returns to its original position. The gas movement diagram shows how the density of the gas behind the flame front is decreased. Figure 19 was derived according to Midgley's method; the calculations, however, are based on an actual pressure curve using values of n for the actual explosion process, as calculated in Section 6.

VII. Conclusions

35. *Summary of Conclusions.*—

(a) The theoretical analysis, as proposed by Nägel and as adapted to the particular cylindrical bomb explosion apparatus used, gives results which conform approximately to the experimental results as determined by photographing the flame propagation.

(b) The theoretical flame propagation curve in most cases differs from the experimentally determined curve by amounts which can be accounted for by the heat loss which occurs in the experimental determinations.

(c) The experimental results on the whole confirm the results of Woodbury, Lewis, and Canby, that the flame fills the bomb at the time that maximum pressure is attained. However, this does not always appear to be the case.

(d) The experimental results do not furnish any evidence of the dependence of the velocity of flame propagation on the initial temperature.

(e) The flame arrest phenomenon appears in all the flame photographs, and occurs quite uniformly at about one half the length of the bomb from the ignition point. At the time of the flame arrest the pressure had in general risen to about 25 per cent of the maximum.

*Jour. S. A. E., vol. 10. p. 357. 1922.

(f) The hypothesis that the flame arrest was caused by spherical pressure waves, or such waves reflected from the walls of the side bomb, has been disproved.

(g) The hypothesis that the flame arrest was caused by a sound wave reflected from the end of the bomb opposite the ignition point has been disproved.

(h) A suggested hypothesis for the cause of the flame arrest is that the great decrease in density of the gases within and behind the flame front causes a momentary extinction of the flame. This explanation at least does not conflict with any known facts regarding the flame arrest.

(i) From the characteristics of the expansion and compression of the burned and unburned gases, respectively, during an explosion, the existence of afterburning and adjustment of chemical equilibrium behind the flame front has been demonstrated.

(j) The relative proportion of the total flame velocity which is due to chemical reaction velocity, for the mixtures investigated, varies from 15 to 85 per cent during the progress of the explosion.

(k) The results indicate that the reaction velocity is a function of the pressure. An equation expressing this relation has been suggested.

Appendix A

Bibliography on Gaseous Explosions

1. *General Statement.*—The following bibliography is a continuation of that published in Bulletin 133 of the Engineering Experiment Station, 1922. It contains references dating from 1919 until 1925. The serial numbers preceding each reference in the bibliography constitute a continuation of the serial numbers used in the earlier list. The references included deal not only with the physical phenomena involved in the explosions of gaseous and liquid fuels, but also with the chemical nature of the reactions. A number of references of a mathematical nature and also some few references relative to instruments and methods used in explosion investigations have also been included.

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